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AMERICAN CHEMICAL SOCIETY
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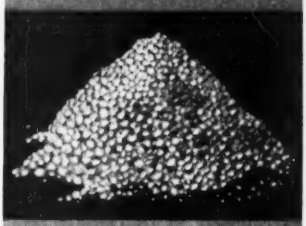

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****Determined according to a modification of ASTM method D 1043-49T. The temperatures shown are the values at which the absolute torsional moduli are 10,000 p. s. i. Although the specimens were still quite flexible, G10,000 was arbitrarily chosen as the stiffening point.**

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THE HISTORY OF THE RUBBER INDUSTRY—No. 1

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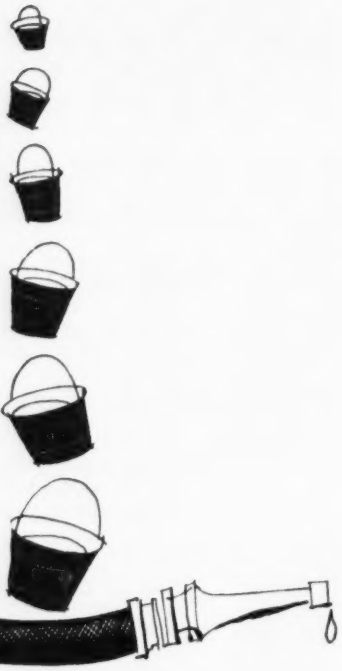

Answer: Two years.

Rubber fire hose first helped relieve the bucket brigade at Fresh Wharf, during the famous London Fire in 1827! The manufacture of rubber fire hose was begun in Manchester, England, just two years earlier, in 1825. Its inventor is reported to be Thomas Hancock, who started the first rubber factory in England in 1820.

In the United States, the manufacture of rubber fire hose was started in Boston, about 1847.

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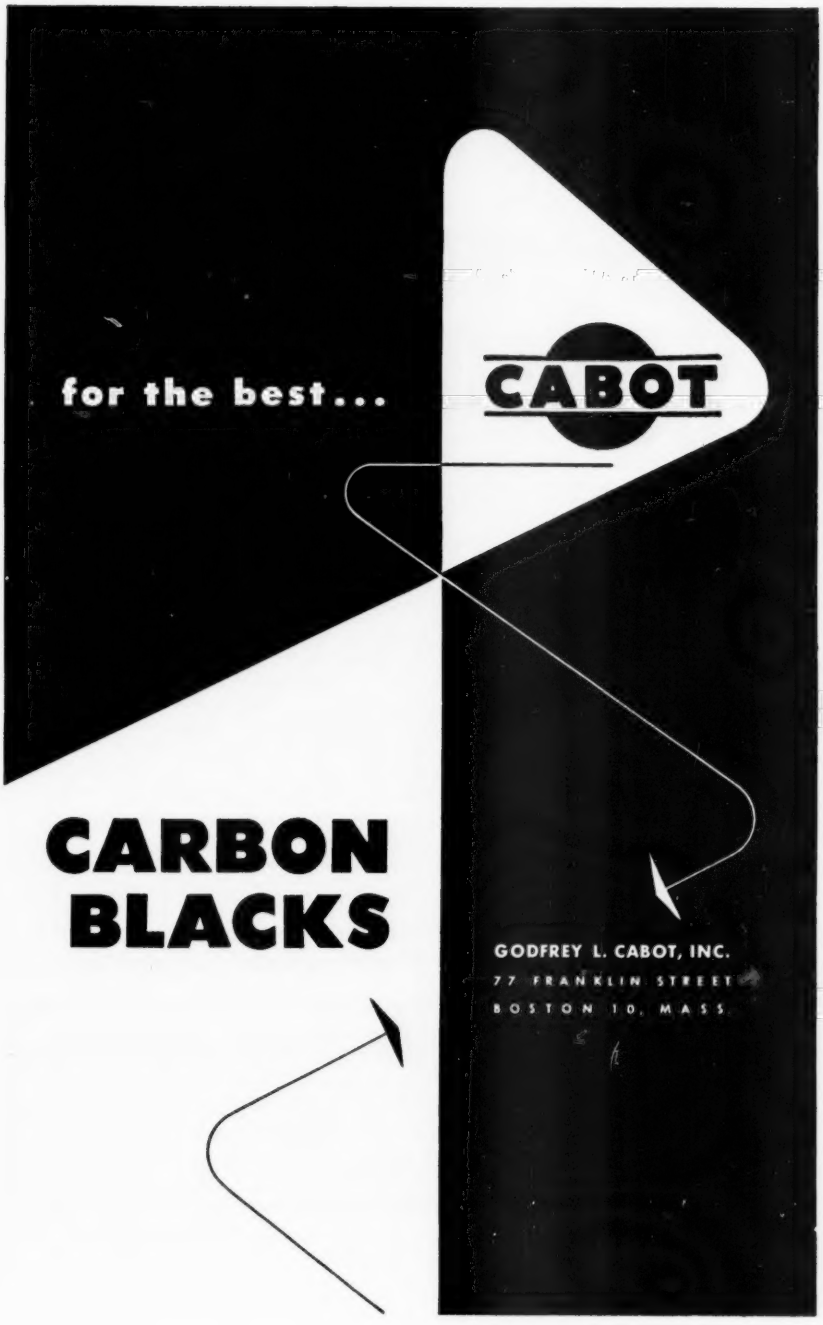
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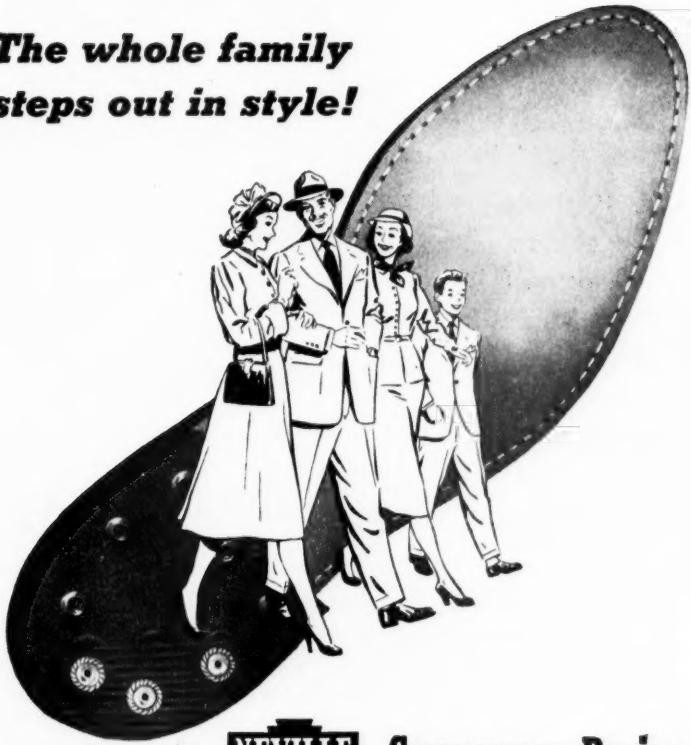

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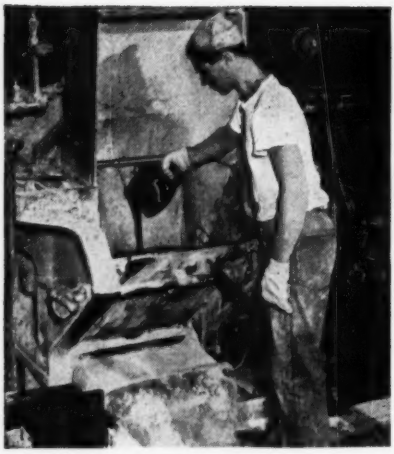

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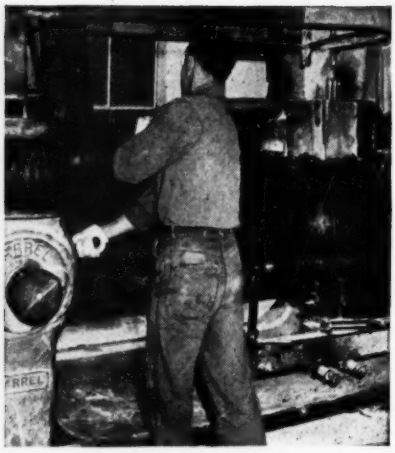

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RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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The AKRON, CONNECTICUT, LOS ANGELES, NORTHERN CALIFORNIA, RHODE ISLAND, and SOUTHERN OHIO Groups have not reported to RUBBER CHEMISTRY AND TECHNOLOGY the election of any officers since those published in the October-December issue of RUBBER CHEMISTRY AND TECHNOLOGY.

NEW BOOKS AND OTHER PUBLICATIONS

HEVEA: THIRTY YEARS OF RESEARCH IN THE FAR EAST. By M. J. Dijkman. (With a Forward by R. D. Rands.) Published by University of Miami Press, Coral Gables, Florida $8\frac{1}{2} \times 11$ in. 330 pp. $6.00.—Ever since Sir Henry Wickham brought Hevea rubber seeds to England from Brazil, which eventually led to the development of the plantation rubber industry in the Far East the literature devoted to the cultivation of rubber has mounted steadily. Both the British and Dutch governments heartily endorsed the distribution of technical booklets and manuals devoted to the subject especially where native producers were involved. Unfortunately, however, this literature is w dely scattered and preponderantly in the Dutch linguage. Accordingly this book, which summarizes the 30 years of Dutch East Indian rubber research up to its sudden stoppage in 1941 by the Japanese occupation, is a most welcome addition to the technical literature on rubber, particularly in view of the current effort to cultivate rubber in the Western Hemisphere.

As Rands points out in his foreword to the book, the work is much more than an accurate chronological summary of the literature in the 30-year period referred to above. It presents critical interpretations of the research results classified under the usual major topics, which facilitates their adaptation to Western Hemisphere conditions, making them more useful than the instructions contained in the British rubber planting manuals, practically all of which are intended for their own special conditions. For example, considerable data on leaf blight is presented, this disease being one of the greatest problems faced by producers of natural rubber in the Western Hemisphere. The scope of the book can be realized from the fact that there are 116 illustrations and 93 tables.

The book has seventeen chapters: (1) Introduction;(2) Historical; (3) Hevea as a Factor in the Economic Development of the East Indies; (4) Development of Rubber Research in Indonesia; (5) Fertiliz ng and Soil Management; (6) Planting Material; (7) Growth; (8) Tap and Tapping Systems; (9) Mechanism of Production and Related Phenomena; (10) Growth, Yield and Disease in Relation to P'anting Density; (11) Diseases and Pests; (12) Outline of Vegetative Selection; (13) Outline of Generative Selection; (14)

Results of Mother-tree Selection;(15) Experimental Results with Vegetative and Generative Selection; (16) Clones and Selected Seedlings Under Commercial Conditions; (17) Ecology and Rubber Improvement. Both author and subject indexes are included as well as an extensive appendix.

The author is well qualified to have undertaken the task of preparing this important work He has been closely identified with the agricultural problems of the Far East since being graduated from the University of Utrecht in 1934 with a Ph.D. in plant physiology. He has been associated with the Un versity of Miami since 1947. [From *The Rubber Age* of New York.]

THE PHYSICS OF RUBBER ELASTICITY. By L. R. G. Treloar. British Rubber Producers' Research Association. Demy 8vo 264 pp., with half-tone frontispiece and 115 text-figures. $6.00.— In both its theoretical and its experimental aspects the subject of the elasticity of rubber has developed in a remarkable manner during recent years. The present volume is an attempt to set down as concisely as possible the essential lines of these advances. The statistical or kinetic theory of elasticity is developed *ab initio*, and is shown to give a satisfactory account of the fundamental mechanical and photoelastic properties of rubber. The book also includes a discussion of the phenomena of cyrstallization, stress relaxation and flow, dynamic properties of rubber, and solution of engineering problems involving large elastic deformations.

"The whole theory of rubber elasticity has never before been discussed so simply and yet so authoritatively as in the present work. Dr. Treloar's command of his subject, coupled with a delight in plain Engl sh, makes his book a pleasure to read, and there is no doubt that it will be for many years an inspirat on to all who strive with rubber. The rubber technologist is presented with a comprehensive working theory in concise form, on which he can soundly develop his approach to his more practical everyday problems" [From the *India-Rubber Journal.*]

DIE POLARNATUR DES KAUTSCHUK (Polar Nature of Rubber). By H. Feuchter. Berlin: Verlag für Radio-Foto-Kinotechnik G.m.b.H., *Kautschuk und Gummi*, 1952, pp. xvi + 208 + 48 diagrams. DM15; 32s. 6d postfree from London.—In this book, the author describes his own conclusions and reports hitherto unpublished experiments in support of his ideas on the structure and elastic behavior of rubber, gutta-percha, and balata. As a chemist, he has attempted to correlate the properties of rubber with a chemical formula; as the discoverer of the racking effect, his practical work has given him the opportunity to examine the elastic properties of stretched cooled raw rubber. In his investigations, he used two types of rubber: "native" rubber prepared by evaporation of latex at room temperature, and purified "total rubber hydrocarbon" prepared by diffusion of native rubber solutions and by subsequent extraction with acetone.

Among other observations, it was found that rubber may be cold drawn to eight times its original length and that the changes due to the swelling of rubber in solvents increase the original linear dimensions by a factor of four. These results were interpreted by assuming that crude rubber is made up of isoprene residues with terminal triple bonds, *i.e.*, with a carbon skeleton corresponding to asymmetrical butadiene. The terminal triple bonds of eight of these residues are joined in spherical configuration to form an octacarbon complex. The other ends of the residues are linked by single bonds to the next asymmetrical butadiene skeleton whose terminal carbon atoms with asymmetrical triple bonds form part of another octacarbon complex. The links between the

octacarbon complexes thus correspond to asymmetrical octatriene chains. The basic lattice element of rubber includes twelve of the octacarbon complexes and the corresponding number of links, in three dimensions. The volume of the spherical aggregate, comprising the octacarbon complex with the attached chains and containing eight butadiene skeletons, is eight times as large as the volume of tightly packed butadiene skeletons which form the octaisoprene unit in crystalline rubber.

It is, therefore, possible to stretch each linear dimension of crystalline rubber to twice its original length in order to form the spherical complex. The space between the octacarbon complexes is taken up by the octatriene chains. If these chains can move in an ellipsoidal free space, and if the fixed points of the chains, *i.e.*, the triple bonds linked in the octacarbon complex, are at the foci of an ellipsoid which has a major axis twice as long as the interfocal distance, then orientation of all the bonded chains, together with orientation of the sides of the spherical complex, leads to a total linear elongation of the rubber to eight times its original length. The ellipsoidal free space is the elastic space.

With this lattice as the fundamental structural unit of crude rubber, it is possible to illustrate the stretched state, the process of crystallization, the stretching of crystallized rubber, the breakdown of the octatriene links to butadiene links during mastication, and the modified lattice in plasticized rubber. When the three-dimensional lattice valencies cannot function, as in very thin sections of rubber, the polar valencies exert an optimum effect.

An experiment is reported in which very thin rubber threads were stretched, by racking, to one million times their original length. When the maximum elongation was thus obtained, there was a sudden stiffening, and the threads then disappeared. The polar forces are due to the electron distribution in the asymmetrical butadiene skeleton.

A large number of phenomena are discussed in this book and explained in terms of the author's structural and polar theories. The theories are applied to gutta-percha isomerism, vulcanization, the effect of softeners, thin-rubber phenomena, crystallization, rubber derivatives, swelling, morphology of rubber, shell aggregation of lattices in liquid and solid surroundings, single phase constitution of rubber, wave theory in relation to elastic motion, the effect of fillers, reinforcement, bond rubber, gel rubber, and the isoelastic state.

The book is not easy reading, despite the excellent diagrams. The author occasionally strays into unrelated fields, such as the polar nature of heat, the structure of snow crystals, and the polar character of aromatic compounds. Nevertheless, the effort required in the study of the book is rewarded by the realization that the rubberiness of rubber can be explained in terms of a chemical model. [From the *India-Rubber Journal.*]

POLYMERISATIONS-KINETIK. By L. Küchler. Göttingen Springer-Verlag, Berlin W 35, Germany. 1941. viii + 287 pp. 16 × 23.5 cm. Price, DM 36.60.—Progress toward understanding the mechanism of polymerization reactions has been fairly steady during the past several decades, but it is only in the last five years that a coherent and inclusive picture has emerged. Consequently, and since there have been no other modern summaries of the general kinetics of polymerization (though the special subject of copolymerization has been treated in a recent book and a noteworthy review) the appearance of the present monograph by Küchler is timely. Since the presentation is scholarly and well-balanced, it is also important.

The content of the book is restricted to the scientific principles of polymerization kinetics, distinct from their technological applications, and in general the viewpoint is that of the physical chemist. The introductory section of 29 pages is composed of two parts, the first a description of the common synthetic polymers and their various structural features, the second a concise summary of the principles of chemical kinetics. There follows the principal section of 220 pages, which treats of addition polymerization under the following chapter headings: I. Experimental Methods. II. Formal Kinetic Treatment of Polymerization Reactions. III. The Free-Radical Mechanism (including copolymerization and emulsion polymerization). IV. The Ionic Mechanisms. The final section of 27 pages deals in more cursory fashion with polycondensations.

Citation of the original literature has been carried through 1950 and is very thorough. The references are given alphabetically at the ends of chapters or subchapters, thus obviating a general author index. A glossary of symbols and an ample subject index conclude the volume.

The general organization of the topics seems excellent, as does the author's selection of numerical and graphical examples from the literature. There is no evidence of the insularity that apparently infects even some Western scientists. The reviewer's high opinion of this work, however, derives from his perusal of certain sections dealing with subjects that demand sound physical exposition and critical judgment. It is quite clear, for example in the paragraphs on thermal polymerization, the nature of the termination step, or the mechanism of emulsion polymerization, that the writer has not merely transcribed the statements of others but has digested them and then presented his own considered synthesis.

The chief sin of omission would seem to be neglect of the kinetics of polymer degradation. This was perhaps because of space limitations, but even a brief description of the depolymerization studies by Melville, Dainton and others would greatly have improved the focus of the general picture.

In summary, this book is strongly recommended to all students and practitioners of polymer chemistry to whom the rather high price (about $8.50) and the language are no great obstacles. [From the *Journal of the American Chemical Society.*]

STYRENE: ITS POLYMERS, COPOLYMERS AND DERIVATIVES. Edited by R. H. Boundy and R. F. Boyer. Reinhold Publishing Corp., 330 West 42nd St., New York 36, N. Y. 6½ × 9 in. 1340 pp. $20.00. (A.C.S. Monograph No. 115.)—Several months ago the first comprehansive book on butadiene was issued, *i.e.*, "Light Hydrocarbon Analysis". It was inevitable that a sister publication covering styrene be published, and the current book amply fills in the data. It is the first complete treatment of styrene to be published, and contains a complete account of the polymerization, copolymerization, chemical modification and manufacture of the material, as well as of its industrially important derivatives.

Starting with a history of styrene monomer and polymer dating back about 100 years, the book describes current methods of manufacture, followed by detailed chapters on physical properties, methods of handling and analysis, and the chemistry of styrene. The theory and practice of styrene polymerization is discussed, with a brief chapter on the uses of styrene monomer, including its role in the synthetic rubber program. The remainder of the book deals with the physical behavior of polystyrene, styrene derivatives and resins, German

styrene practice and copolymers of styrene, and concludes with a lengthy description of the fabrication of polystyrene.

The twenty-two chapters include: (1) History; (2) Manufacture of Styrene Monomer; (3) Physical Properties of Styrene Monomer; (4) Chemistry of Styrene Monomer; (5) Analysis of Styrene Monomer; (6) Handling Styrene Monomer; (7) Polymerization of Styrene; (8) Summary of Uses for Styrene Monomer; (9) Molecular Weight and Solubility of Polystyrene; (10) General Physical Properties of Polystyrene; (11) Optical and Electrical Properties of Polystyrene; (12) Rheological Properties of Polystyrene; (13) Degradation of Polystyrene; (14) Chemical Alteration of Styrene Polymers; (15) Alpha-Methylstyrene; (16) Ethylvinylbenzene and Divinylbenzene Mixture and Its Copolymers; (17) Halostyrenes and Other Vinyl Aromatic Compounds; (18) Styrene Resins; (19) A Survey of Styrene and Polystyrene in Germany; (20) Copolymerization; (21) A Survey of Patent Literature on Styrene Copolymers; (22) Fabrication of Polystyrene; [From *The Rubber Age* of New York.]

FUNDAMENTAL PRINCIPLES OF POLYMERIZATION: RUBBERS, PLASTICS AND FIBERS. By G. F. D'Alelio. John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y. 6 × 9¼ in. 518 pp. $10.00.—Numerous publications have appeared in recent years on the subject of polymerization, but most of these books treat with the technology of applied polymerization, namely, the field of plastics. The current book, which deals with the fundamental principles of polymerization, is thus a most welcome addition to the technical literature. It is not encyclopedic in scope, but does summarize the minimum fundamental knowledge that a scientist in the field of polymerization requires.

The book is divided into 10 chapters. It begins with a discussion of the gaseous, liquid, and solid states of matter, then classifies polymers according to the rubber, plastic and fiber states. Polymerization reactions and functionality are discussed, followed by a critical analysis of the "existence" of macromolecules. The nonhomogeneity of polymers and their properties are treated, and important intermolecular and intramolecular reactions summarized, followed by details on the polymerization processes, and an outline of the basic ones. The last four chapters deal with molecular weight determinations, the kinetics of polymerization, reaction loci in polymerization systems, copolymer compositions, and the stability of polymers. [From *The Rubber Age* of New York.]

NATURAL RUBBER LATEX AND ITS APPLICATIONS: I—AN INTRODUCTION TO ITS ORIGIN, PROPERTIES AND MANUFACTURE. By Henry P. Stevens. British Rubber Development Board, Market Buildings, Mark Lane, London, E.C.3, England. Available from Natural Rubber Bureau, 1631 K St., N.W., Washington 6, D. C. 5½ × 8½ in. 72 pp.—Volumes on latex, in one form or another, have been issued from time to time by the British Rubber Development Board or its predecessor organizations since 1928, the last edition in 1948. Based on advances in recent years in both the theoretical and practical fields, it was realized that a new revision was required. However, so many changes were called for in the text that a complete rewriting was necessary and so many new applications have been developed that it was impractical to combine all in one volume. Accordingly, the Board decided to issue a series of books on latex, of which the current volume is the first. Subsequent volumes will cover specialized applications.

The current work is devoted to the origin, properties, and manufacture of latex. and is divided into seven chapters: (1) Botanical Sources; (2) Con-

stituents of Latex and Their Effects; (3) Properties and Testing; (4)Concentration; (5) Applications of Latex: Production of Rubber Goods; (6) Patents; (7) Bibliography. The chapter on "Patents" includes a list of short abstracts from British patents; that on "Bibliography" contains a short list of books and periodicals devoted to latex. [From *The Rubber Age* of New York.]

CHRONOLOGICAL LIST OF TECHNICAL PAPERS RELATING TO THE GOVERNMENT SYNTHETIC PROGRAM. Compilation DRP-4. Research & Development Division, Office of Synthetic Rubber, Reconstruction Finance Corp., 811 Vermont Ave., N.W., Washington 25, D. C. 66 pages.—This compilation gives a chronological listing of papers dealing with work supported by RFC. The listing is by company or organization, and each paper is shown by title, author, publication, and date of publication. A separate 16-page author index for this compilation is also available. [From the *India Rubber World.*]

BIBLIOGRAPHY OF RUBBER LITERATURE FOR 1944 AND 1945. Division of Rubber Chemistry, American Chemical Society. Division treasurer—A. W. Oakleaf, Phillips Chemical Co., 605 Evans Bldg., Akron 8, O. Cloth, 6 × 9 inches, 415 text pages. Price to nonmembers, $5.—This seventh edition of the "Bibliography" brings the total coverage of the series to the period 1935–1945. The new book continues the growth in size noted in the previous edition, being some 100 pages larger. The current edition contains 4903 specific references to patents and literature, compared with 3,856 references in the 1942–1943 edition. The general format remains the same; the references are classified in 123 groups, and brief abstracts appear for most references. There are also comprehensive author and subject indexes. The value of this work to all technical men in the rubber field requires no elaboration. [From the *India Rubber World.*]

RUBBER—FOURTH ANNUAL REPORT BY THE SECRETARY OF COMMERCE. U. S. Department of Commerce. United States Government Printing Office, Washington 25, D. C. 20¢. 48 pages.—This report for the period July 1, 1951 to June 30, 1952, required by the Rubber Act of 1948, includes a review of operations under this Act of the President and the Congress. No new information is contained in the booklet, which has sections on such subjects as "International Framework of U. S. Rubber Operations", "Synthetic Rubber Plant Expansion and Prices", and "United States Rubber Position". Nineteen tables on production, consumption, and stocks of natural and synthetic rubbers, tires and tubes, etc., through June, 1952, are useful for future reference. [From the *India Rubber World.*]

FLUID RUBBER COMPOSITIONS: THEIR PREPARATION AND APPLICATIONS. (Broadsheet No. 2.) Rubber Technical Developments, Ltd., 78 Bridge Road East, Welwyn Garden City, England. 8½ × 11 in. 6 pp.—The term *fluid rubber*, in this instance, covers compositions containing neither water nor volatile solvent, which can be poured and set to form elastic soft rubber or hard rubber articles. The principles underlying the preparation of these compositions, the types of end products that can be obtained, and the applications for such products are described in this report. Among products discussed are printer's rollers, battery boxes and various molds for plaster casting. Among preparations discussed are those based on "20 Mooney" rubber, Rubbone-N,

and Rubbone-N and depolymerized rubber. [From *The Rubber Age* of New York.]

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY. Vol. XV, 1951. Edited by T. J. Drakeley. W. Heffer & Sons, Ltd., Cambridge, England, for the Institution of the Rubber Industry, 12 Whitehall, London S.W. 1, England. Cloth, $7\frac{1}{2} \times 9\frac{3}{4}$ inches, 142 pages. Price, 1/1/0.—This latest book in the series consists of 22 articles on developments during 1951 in the following fields: planting and production of rubber and latex; latex properties and applications; rubber physics and chemistry; synthetic rubber; testing equipment; compounding ingredients; fibres and fabrics; properties of vulcanized rubber; tires; belting; hose and tubing; cable and insulation; footwear; mechanical goods; games, sports accessories, and toys; surgical goods; textile-rubber composites, solvents, and cements; cellular rubber; hard rubber; flooring; and machinery and appliances. A historical and statistical review article is also included, and there are name and subject indexes. [From the *India Rubber World.*]

ENCYCLOPEDIA OF SURFACE-ACTIVE AGENTS. By J. P. Sisley. Translated and revised by P. J. Wood. Published by Chemical Publishing Co., Inc., 212 Fifth Ave., New York 10, N. Y. 6 × 9 in. 540 pp. $15.00.—This is a combination text-book and directory. It is divided into two parts, the first dealing in text-book form with the general aspects of surface-active agents, their properties, applications and methods of manufacture; the second consisting of an alphabetical listing of brand-name surface-active agents manufactured all over the world. Among the chemicals covered in the first part are wetting agents, detergents, penetrants, foaming compounds, emulsifiers, and dispersing agents. Their many applications in numerous industries, including the rubber industry, are discussed. An efficient system of classifications by which every variety of the modern surface-active agents can be identified by simple symbols is included. [From *The Rubber Age* of New York.]

DIRECTORY OF THE INTERNATIONAL RUBBER INDUSTRY. Verlag fur Wirtschaftsliteratur, G.m.b.H., P.O. Box 121, Zurich 55, Switzerland. Available from Swiss American Advertising Co., 1910 Marmion Ave., New York 60, N. Y. $6\frac{1}{2} \times 9$ in. 416 pp. $12.00.—There has long been need for an international directory covering the rubber manufacturing industry, a need which goes a long way toward fulfillment by the publication of this work, the first attempt at world-wide coverage. Since it is a first attempt, and because of the enormity of the job, there are some definite improvements called for, and it is to be hoped these improvements will be made in any subsequent edition planned by the publishers.

The major portion of the directory is devoted to listings of rubber manufacturers in various countries, grouped by areas, including Europe, North America, South America, Central America, Africa, Asia, Australia, and New Zealand; a total of 70 countries. The listings cover company name and address, type of goods produced and, where possible, the number of workers employed. No attempt is made to include data on company personnel, one of the main features of such national directories as the "Rubber Red Book" or the "Rubber Trade Directory of Great Britain."

In view of language difficulty, the products shown for companies in various countries appear in either English, French, or German, although in some cases

they are indicated under separate listings in more than one language, the second one generally English. Recognizing this problem, the publishers have included a glossary of rubber products and terms in the three languages used, these glossaries covering German-English-French, English-German-French, and French-German-English. Inclusion of the glossaries made it possible to avoid printing the detailed products of each firm in three languages although presenting the details in this manner would have been of considerable help to users of the directory.

A rather odd system is used in the listing of companies for each country. Instead of using a straight alphabetical system, the companies are arranged "in alphabetical order by localities". This means that the names of cities in which the companies are located were used as an alphabetical guide. This makes it somewhat difficult to locate any specific company in any particular country unless the user is aware of the exact city or town in which the company is situated. In the case of the United States, for example, listing of the companies by states would have been a preferable method. In all cases, a straight alphabetical list by companies would seem to be the better method.

In addition to data on rubber manufacturers, the directory includes a list of suppliers of rubber chemicals, compounding ingredients, machinery, etc., presumably on a world-wide basis. This section covers only some 20 pages and could stand considerable expansion. Other sections are devoted to lists of schools and research laboratories, professional organizations, and professional journals.

Despite these obvious shortcomings, this international rubber directory is a welcome addition to the industry's store of knowledge, and should prove a valuable adjunct to international trade. [From *The Rubber Age* of New York.]

TECHNICAL REPORTING. Joseph N. Ulman, Jr. Henry Holt & Co., Inc., 383 Madison Ave., New York 17, N. Y. Cloth, $6\frac{1}{2} \times 9\frac{1}{4}$ inches, 303 pages. Price, $4.75.—This volume gives extremely practical information on how to convey information and ideas accurately and efficiently. Major emphasis is placed on preventing one of the commonest and most serious faults in technical writing, the burying of important ideas under a mass of detail. Accordingly, the author discusses only the principles that are most overlooked by technical writers and does not give a comprehensive academic treatment of grammar and punctuation rules other than those which can be easily remembered by general rules of thumb. Clarity and understanding of the principles discussed are enhanced by the inclusion of many passages taken from technical papers or reports, with the author giving both the original example and suggested revision in each case.

The first portion of the book covers basic issues, including the importance of proper technical reporting, fundamental principles, and general procedure for preparing a report. Different forms of reports, including laboratory, formal, informal, and oral, and technical papers, are described in the second part. The third and concluding section deals with writing style, grammar, punctuation, mechanics, use and preparation of tables, and visual presentation of information. An appendix gives standard abbreviations for technical terms; specimens of different type of reports; and a bibliography for further reading. A subject index is included. [From the *India Rubber World.*]

Publications of the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa. 1951 SUPPLEMENT TO BOOK OF ASTM STANDARDS, INCLUDING TENTATIVES. Part 5, Textiles, Soap, Fuels, Petroleum, Aromatic Hydrocarbons, Antifreezes, Water. Paper, 6 × 9 inches, 339 pages. Price, $3.50. Part 6. Electrical Insulation, Plastics, Rubber. Paper, 6 × 9 inches, 248 pages. Price, $3.50.—Parts 5 and 6 of the Supplement present 41 and 33 standards, respectively, covering products, test methods, and definitions of terms.

1951 INDEX TO ASTM STANDARDS. Paper, 6 × 9 inches, 282 pages.—This booklet gives both subject and numerical indices of the 1,106 standards and 704 tentatives in effect as of December, 1951. A listing of other Society publications is also included. [From the *India Rubber World.*]

ASTM STANDARDS ON TEXTILE MATERIALS. American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6 × 9 in. 660 pp. Heavy paper cover. $5.00.—This new compilation of textile standards includes, in their latest form, 99 specifications, test-methods, and tolerances developed by ASTM Committee D-13 on Textile Materials. In addition to the standards, extensive sections give photomicrographs of common textile fibers and photographs of defects in woven fabrics, a glossary of textile terms, and terms relating to hand of fabrics. Two technical papers are also included, one on "An Application of Statistics to Quality Control in the Textile Industry", the other on "Statistical Considerations in Fiber Research". A convenient table of contents is provided (by subject and A.S.T.M. serial designations), and an extensive index. [From *The Rubber Age* of New York.]

MOONEY VISCOSITY CHANGES IN FRESHLY PREPARED RAW NATURAL RUBBER *

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INTRODUCTION

In the scheme for the technical classification of natural rubber, assessment of processability has been based on Mooney viscosity determinations on the freshly prepared raw material[1]. Consumer evaluations of supplies of technically classified ribbed smoked sheet from the Far Eastern producing areas have shown, however, that this method is not particularly satisfactory, due in part to increases in Mooney viscosity which occur between initial testing in the producing areas and use by the consumer[2].

In 1927 de Vries[3] reported changes in hardness of first grade rubber on storage, and associated hardening and softening, respectively, with an excess or deficiency of serum substances. Investigation into the effect of different storage conditions on the hardness of raw rubber were carried out by Martin and co-workers[4] in 1930–31, and they concluded, *inter alia*, that temperature of storage, complete absence of moisture, and presence of oxygen all had a permanent effect on the hardness of rubber as measured by a parallel-plate plastometer. More recent work by various investigators[5] has confirmed that the Mooney viscosity of "old" rubber, *i.e.*, rubber as received by the consumer after normal shipment from the producing areas, can be varied by some four to ten units, depending on whether it is stored at high (98 per cent) or low (0 per cent) humidity for a further period.

From the point of view of any classification scheme based on measurements of Mooney viscosity, the important changes are those which take place between the testing of the freshly prepared rubber under tropical conditions and its use by the consumer after storage, usually in a temperate climate. Wren[6] observed increases of the order of 25 Mooney units for freshly prepared ribbed smoked sheet when stored for three months over calcium chloride, compared with increases of about five units when stored for the same period in a laboratory under tropical conditions, and the work reported in this paper covers some of the conditions which influence Mooney viscosity and hardness changes in fresh rubber during subsequent storage. It was carried out mainly for the purpose of obtaining information on Mooney viscosity changes during storage in connection with the scheme for the technical classification of natural rubber, and it is presented here, not as a completed investigation, but as a series of observations which it is hoped may serve to indicate the lines of development of further research.

SAMPLE PREPARATION AND TEST METHODS

The rubbers used throughout were freshly prepared, *i.e.*, tested not later than two weeks after preparation, ribbed smoked sheet or air-dried crepe. For

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each experiment, a homogenized mass was obtained by mill blending, using six passes between the cold rolls of a 12 × 6 inch laboratory mill, at friction ratio (1:1.4), the sample being rolled and up-ended between passes. It had previously been established that this method gave satisfactory blending, with a minimum of breakdown of the raw rubber. After blending samples were sheeted out to the desired thickness by one additional pass.

Mooney viscosity determinations were carried out on an N.B.S. model Mooney viscometer at 100° C, using a large (1½ inches diam.) flat cross-hatched rotor. Samples were allowed to warm up for one minute in the instrument, and readings were recorded after four minutes' shearing. The standard error of testing for a single Mooney determination was 0.7 unit. The Mooney values recorded in Tables I, III, IV, and V are the means of duplicate determinations on different test-portions taken from the same sample.

Plasticity and recovery values were determined, using a Williams parallel-plate plastometer operating at 100° C. Plasticity numbers were recorded on spheres of 2 cc. capacity after ten minutes' application of the load. Recovery was measured after ten minutes' recovery at 100° C, followed by fifteen minutes' cooling at room temperature. The values recorded in Table V are the means of duplicate determinations on different portions from the same sample, and the Standard Error of testing for a single determination was 0.06 mm. for plasticity and 0.09 mm. for recovery.

The samples were stored in glass containers. The samples were in the form of sheets of approximately 25 grams, and of varying thicknesses depending on the experimental conditions. Controls were stored in the laboratory under tropical conditions (temperature 30 ± 3° C; relative humidity 75 per cent ± 15 per cent), but in the absence of direct sunlight. For experiments at higher temperatures, samples were stored in containers in electric thermostatically controlled air-convection ovens.

Weight change data were obtained from separate portions of the samples under investigation, of weight approximately 5 grams, and all changes in weight are based on the original weight of the samples under investigation. The Standard Error of a single weight change determination was 0.01 per cent.

Acetone-extracted samples were prepared by continuous extraction with cold acetone under nitrogen for twelve hours.

Deproteinized rubber was produced by multiple creaming of fresh latex with ammonium alginate, in the presence of ammonium oleate.

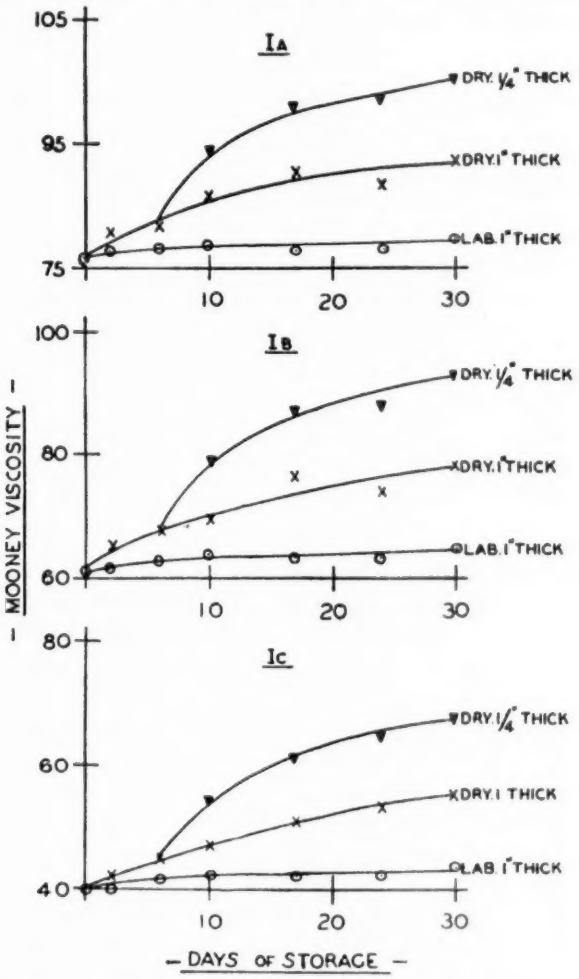
EXPERIMENTAL PROCEDURE AND RESULTS

STORAGE AT LOW RELATIVE HUMIDITY

Influence of sample thickness.—Since the extent of drying-out of a thick sample of rubber would be less than for a thinner sample under similar conditions, it appeared likely that specimen thickness would also influence the extent of the increase in hardness during storage at low relative humidity. To examine this, portions of a sample of ribbed smoked sheet were broken down by cold milling to give two levels of Mooney viscosity, and the unmasticated rubber and the two masticated samples were stored in approximately 1-inch thick slabs over calcium chloride at room temperature, with controls of the same thickness stored in the laboratory. After six days' storage, portions from the samples kept over calcium chloride were sheeted out approximately ¼ inch thick and storage was continued. Samples were removed at intervals throughout the

storage period and Mooney viscosity determinations carried out immediately after removal.

The results plotted in Figure 1 confirm that a greater increase of Mooney



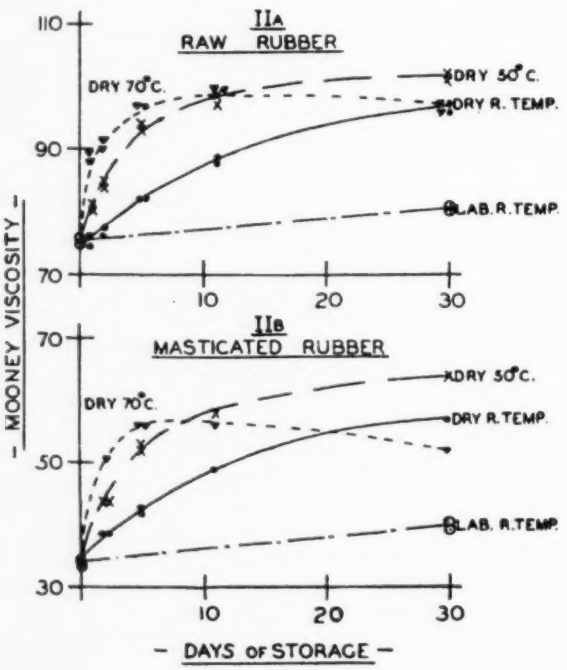
viscosity takes place on dry air storage than on storage under tropical conditions and that, as anticipated, the thinner samples harden more rapidly than the thicker. In these respects, both unmasticated and masticated rubbers behave in a closely similar manner, which indicates that the changes are not restricted to a particular range of molecular weight.

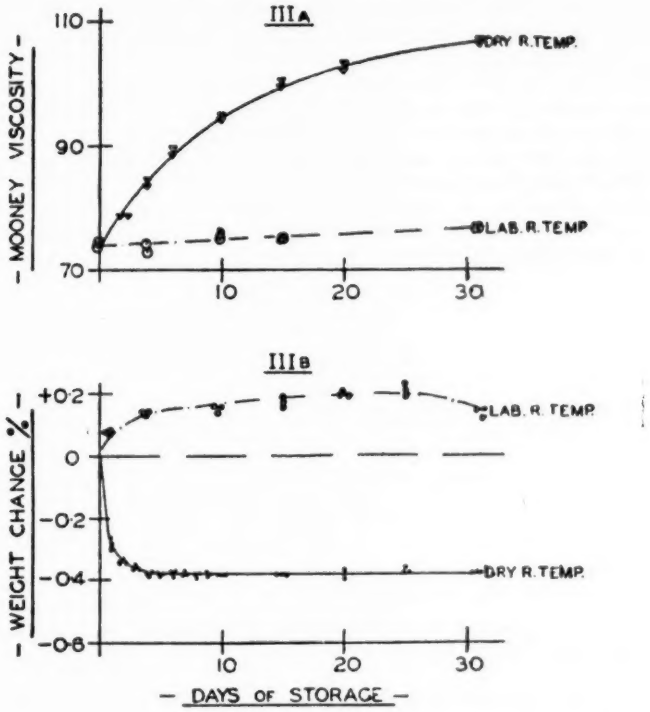
Effect of temperature of storage.—A further obvious factor likely to influence the changes under investigation was temperature of storage. Portions of unmasticated and masticated ribbed smoked sheet rubber approximately $\frac{1}{8}$ inch

thick were, therefore, stored over calcium chloride at room temperature (about 30° C) and at 50° and 70° C. Mooney viscosity changes during one month of storage are shown graphically in Figure 2. In the early stages, the higher the temperature the greater the Mooney increase, but oxidative breakdown is apparent on prolonged storage at 70° C, and masks the hardening effect.

TABLE I

	Stored over calcium chloride			Laboratory-stored		
Days of storage	Raw Mooney viscosity	Change in weight	Further change in weight of stored sample on oven-drying	Raw Mooney viscosity	Change in weight	Further change of weight of stored sample on oven-drying
0	74.0	—	—	74.0	—	—
1	—	−0.28%	—	—	+0.09%	—
2	78.5	−0.34%	−0.10%	—	—	—
3	—	−0.36%	—	—	—	—
4	84.0	−0.37%	−0.09%	73.5	+0.14%	−0.56%
5	—	−0.37%	—	—	—	—
6	89.5	−0.37%	−0.09%	—	—	—
7	—	−0.38%	—	—	—	—
8	—	−0.39%	—	—	—	—
9	—	−0.37%	—	—	—	—
10	95.0	−0.38%	−0.12%	75.5	+0.18%	−0.62%
15	100.0	−0.38%	−0.07%	75.0	+0.19%	−0.59%
20	103.0	−0.38%	−0.10%	—	+0.20%	—
25	—	−0.37%	—	—	+0.21%	—
31	108.0	−0.37%	−0.07%	77.0	+0.17%	−0.59%





Relationship between Mooney viscosity changes and weight changes.—In view of the large increase in Mooney viscosity of fresh natural rubber on storage at low relative humidity, it was of interest to examine the possible relationship between the Mooney change and the moisture content of rubber. The long period during which the Mooney changes take place, compared with the comparatively short time necessary to dry rubber in an oven, when no marked change in viscosity is apparent, suggested that Mooney changes would continue for a considerable time after constant weight had been reached during drying.

This was confirmed by the results of an experiment where both Mooney viscosity and weight changes were determined at intervals on approximately $\frac{1}{8}$-inch thick samples stored over calcium chloride at room temperature. Control samples stored under tropical conditions were also similarly tested, and, in addition, data were recorded on the further changes in weight brought about by oven-drying to constant weight at 85° C for both the dry-air and tropical-stored samples. Test results are recorded in Table I, and the Mooney viscosity and weight changes for room-temperature drying are shown graphically in Figure 3.

The rubber reaches constant weight over calcium chloride after about five days, but slow Mooney increase is still taking place after thirty days' storage. Since the viscosity changes are apparent from the onset of drying, it is also evident that the rubber does not need to be completely dry before changes can commence.

It is of interest to observe that approximately 0.1 per cent of additional moisture and (or) volatile matter is removed by heating the rubber at 85° C after it has reached equilibrium over calcium chloride at room temperature. In addition, the use of a number of different drying agents indicated that the changes observed were brought about by the removal of moisture and were not dependent on the nature of any particular desiccant.

Purified rubbers.—In considering factors responsible for hardening during low humidity storage, attention was first directed to the nonrubber components. Acetone extraction of natural rubber results in an immediate increase in Mooney value, presumably due to the removal of acetone-soluble substances which act as softeners, but from the data presented in Table II it can be seen

TABLE II

	Raw Mooney viscosity			
	Normal rubber		Acetone-extracted rubber	
Days of storage	Laboratory storage	Storage over calcium chloride	Laboratory storage	Storage over calcium chloride
0	94	95	101	101
1	—	95½	—	102
4	95	98½	102½	194½
6	94½	102½	103	105½
10	95	104	103½	109
14	97	109	105½	112½
21	95	107	104½	112½
29	95½	103	105	114

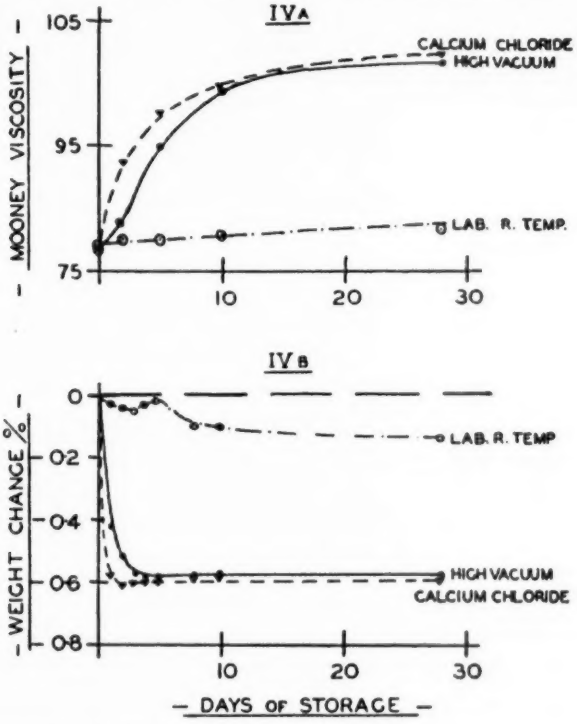
that subsequent drying over calcium chloride produces a further increase which is considerably in excess of that which takes place during storage at high humidity.

The close connection known to exist between the moisture content, rate of drying, and protein content of natural rubber suggested that the changes might be associated with hardening of the nitrogenous nonrubber components and an examination was made of a deproteinized rubber, containing only a very small quantity of residual nitrogen. This material was prepared by repeated creaming of fresh field latex, to which ammonium oleate had been added, using 0.15 per cent ammonium alginate as a creaming agent. The resultant purified

TABLE III

	Deproteinized rubber				Rubber containing casein			
	Laboratory storage		Storage over calcium chloride		Laboratory storage		Storage over calcium chloride	
Days of storage	Raw Mooney viscosity	Weight change	Raw Mooney viscosity	Weight change	Raw Mooney viscosity	Weight change	Raw Mooney viscosity	Weight change
0	56½	—	56½	—	70½	—	70½	—
1	—	−0.09%	—	−0.27%	—	+0.03%	—	−0.47%
2	—	−0.19%	—	−0.33%	—	+0.02%	—	−0.54%
3	—	−0.20%	—	−0.34%	—	+0.04%	—	−0.56%
5	53	−0.27%	78½	−0.36%	73	+0.14%	88	−0.59%
6	—	−0.30%	—	−0.36%	—	Nil	—	−0.58%
9	—	—	—	−0.36%	—	—	—	−0.59%
10	—	−0.34%	—	−0.37%	—	−0.01%	—	−0.59%
13	—	−0.34%	—	−0.36%	—	−0.01%	—	−0.60%
15	—	−0.35%	81	−0.35%	—	−0.30%	90½	−0.06%
20	—	−0.36%	—	−0.35%	—	−0.06%	—	−0.61%
26	50½	−0.34%	76½	−0.34%	72	−0.06%	92	−0.61%

cream was divided into two portions; to one was added a solution of casein in ammonia water to give approximately 0.5 per cent casein on the dry rubber. Both latexes were coagulated with acetic acid, creped approximately $\frac{1}{8}$ inch thick, and allowed to dry in the dark at room temperature. The rate of drying of the rubber containing added casein was noticeably more rapid than that of the purified material; the latter took over three weeks to become translucent, and even then it was necessary to break up patches of very wet material by sheeting out at tight nip. The total nitrogen content of the deproteinized rub-

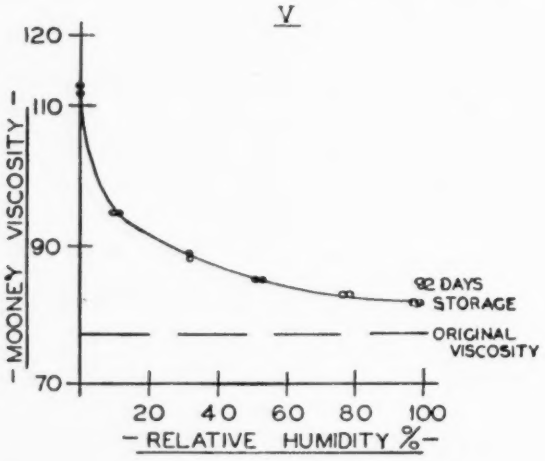


ber was very low, *i.e.*, 0.028 per cent; the rubber containing casein had a total nitrogen content of 0.480 per cent.

Details of Mooney viscosity and weight changes on storage of these materials at low and high humidity are given in Table III. It is evident that the deproteinized rubber had not reached equilibrium with the laboratory conditions at the commencement of the experiment, since loss of weight continued throughout the storage period in the laboratory. Although it is unlikely that there would have been much marked difference in the final moisture content of the deproteinized samples after dry-air and laboratory storage, storage at low humidity still gave a considerable increase in Mooney viscosity, and the behavior in this respect was very similar to that of the samples containing deliberately added casein, and also of samples of normal smoked sheet. Similar conclusions are arrived at for storage of portions of the materials used in the above experiment after acetone extraction. In the case of acetone-extracted de-

proteinized rubber, considerable oxidative breakdown is also apparent during storage, but the main effect of greater hardening at low humidity is not masked, and it is concluded that the major portion of the nitrogenous and acetone-soluble nonrubber components of Hevea rubber are not responsible for the hardness changes brought about by drying.

High-vacuum drying.—Since nonrubber components did not appear to play any part in storage hardening, the function of the rubber hydrocarbon itself was next considered. It seemed possible that either atmospheric oxygen or oxygen dissolved in the rubber might be responsible for continued linear polymerization or, alternatively, the build-up of cross-links, these reactions being accelerated in the absence of moisture. Samples were evacuated on an all-glass high-vacuum line, using a rotary oil pump backed by a single stage mercury diffusion pump. Continuous pumping was carried out for periods of not



less than five hours each day, the samples being sealed off from the line between each evacuation, and after about three days pressures of less than 10^{-4} mms could be maintained.

The results of experiments (Figure 4) show that, although there is a lag both in Mooney increase and weight change during the early stages of vacuum drying compared with drying over calcium chloride (due in all probability to the intermittent nature of the former process in this experiment compared with the continuous removal of moisture over a desiccant), corresponding values for both treatments are of the same order after about ten days' storage. In consequence, it is considered that oxygen is not directly involved in the mechanism.

STORAGE AT DIFFERENT RELATIVE HUMIDITIES

Since the Mooney viscosity of natural rubber did not appear to bear any close relationship to moisture content at any particular instant, it appeared that more valuable comparisons would be those showing hardening after prolonged storage at different relative humidities.

Mooney viscosity and weight change data obtained at intervals throughout a six-months' period, for samples stored at 22° C between 0 per cent relative

humidity and 98 per cent relative humidity are shown in Table IV. Figure 5 is a plot of Mooney viscosity against relative humidity after three months' storage, when Mooney equilibrium has been reached for these particular conditions with samples approximately $\frac{1}{8}$ inch thick. It is evident that the relative

TABLE IV

Relative humidity	10 Days' storage	30 Days' storage		92 Days' storage		182 Days' storage	
	Weight change	Weight change	Mooney viscosity	Weight change	Mooney viscosity	Weight change	Mooney viscosity
0%	−0.35%	−0.36%	105.5	−0.34%	112.5	−0.33%	108.0
10%	−0.30%	−0.30%	88.0	−0.29%	95.0	−0.29%	93.5
32%	−0.20%	−0.20%	83.0	−0.20%	88.5	−0.20%	87.5
52%	−0.03%	−0.01%	81.0	−0.04%	85.5	−0.06%	83.5
79%	+0.37%	+0.42%	80.0	+0.47%	83.0	+0.38%	82.0
98%	+1.22%	+1.76%	79.0	+1.27%	82.5	+0.52%	81.0

Note:—Original Mooney viscosity = 77.5 units.

humidity of storage influences both the rate and the extent of the Mooney increase, and that increases are most marked when storage takes place below about 30 per cent relative humidity.

Weight change data at the higher humidities became unreliable after about thirty days' storage, due to development of mold growth.

ALTERNATE STORAGE AT LOW AND HIGH HUMIDITY

In considering the practical consequences of the hardening of natural rubber, as demonstrated in the above experiments, it was necessary to know whether a permanent change was produced or whether the effect of low humidity storage could be reversed in whole or part by subsequent storage at high humidity.

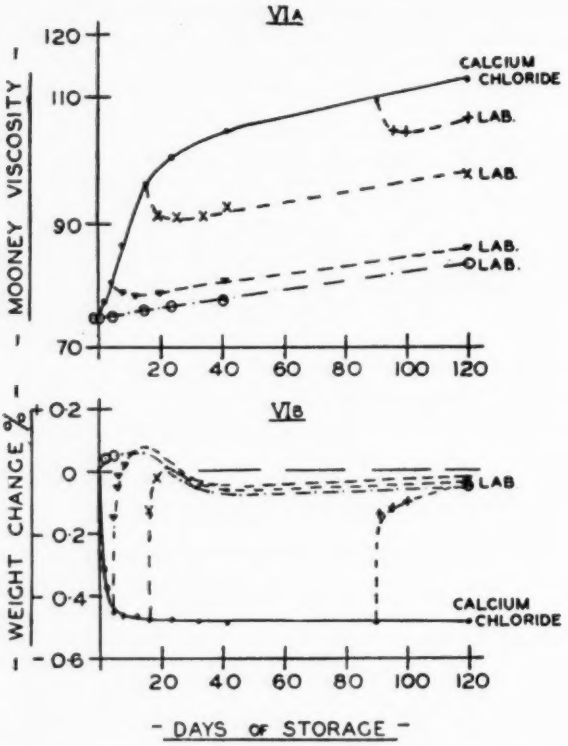
Figure 6 illustrates the effect on Mooney viscosity and weight change of the return of approximately $\frac{1}{8}$-inch thick samples to tropical conditions at intervals throughout a four-months' storage period over calcium chloride at room temperature.

It is evident that only a small portion of the Mooney increase which takes place at low relative humidity can be reversed by further storage under tropical conditions, but despite the large differences shown up by Mooney values, different conditions of storage prior to reaching equilibrium in the laboratory have no significant effect on the final moisture content.

EVIDENCE FOR THE BUILD-UP OF A CROSS-LINKED STRUCTURE

In the course of these investigations, it was noted that there was a marked difference in the behavior of laboratory and dry-air stored rubbers on immersion in benzene. The former passed completely into solution as far as could be determined visually after three days at room temperature without agitation, whereas the latter gave a macrogel structure, with the swollen outline of the original sample shape still readily discernible after more than a week's immersion.

Attempts to apply the Harris Cage technique[7] of gel determination to obtain quantitative estimations of these changes in structure were not particularly successful, because of the high errors of reproducibility which were encountered. However, the method supplied a very definite qualitative indication of gel development, since laboratory-stored materials gave benzene-insoluble



values in the range 2.5 per cent to 6 per cent, whereas low-humidity-stored samples ranged from 25 per cent to 54 per cent.

Comparisons of Mooney viscosity and Williams plasticity values, respectively, under conditions of high and low humidity, confirmed the findings of the earlier investigations with regard to increases in hardness as measured by the parallel-plate instrument during dry storage, but, in addition, very large increases in the recovery values were also observed under these conditions.

Table V gives Mooney and Williams data on samples stored wet and dry at room temperature for a period of three months. The rubber was in the form of

TABLE V

Days of storage	Laboratory storage			Storage over calcium chloride		
	Mooney viscosity	Williams plasticity (mm.)	Williams recovery (mm.)	Mooney viscosity	Williams plasticity (mm.)	Williams recovery (mm.)
0	77.0	4.00	5.02	77.0	4.00	5.02
4	77.0	3.99	5.85	79.0	4.09	5.90
10	77.5	4.35	5.60	84.0	4.43	6.58
15	78.0	4.10	5.88	88.0	4.45	6.51
20	79.0	4.32	6.05	88.0	4.57	6.90
35	80.0	4.39	6.11	98.0	5.15	9.40
60	80.5	4.32	6.37	103.0	5.96	11.35
90	82.5	4.18	5.94	105.0	5.63	11.30

1-inch thick mill-blended slabs to allow curring of the plasticity test-pieces without the need for milling, which might have resulted in some break-down of structure. The increase in the recovery value of 125 per cent for the samples stored over calcium chloride, compared with the increase of only 18 per cent for laboratory-stored material, suggests the development of a lightly cross-linked structure with a consequent increase in "nerve" during storage of rubber in the absence of moisture.

TECHNOLOGICAL PROPERTIES

As mentioned earlier, it is evident that by the time natural rubber reaches the consumer, changes have already taken place to a lesser or greater extent, depending on the time and conditions of storage, and fresh rubber would never be available to a manufacturer unless his factory was situated in a rubber-producing area. It was, nevertheless, of interest to compare the technological behavior of fresh rubber and storage-hardened rubber from the same latex source. The stored rubber for this experiment was prepared by rapid drying

TABLE VI

Laboratory-stored raw Mooney 74.		Stored over calcium chloride raw Mooney 103.	
Mooney after breakdown		Mooney after breakdown	
A	B	A	B
20.5	21.0	28.5	28.0
21.0	20.5	29.0	28.5
20.0	20.0	29.5	30.0

of a portion of a mill-blended sample of ribbed smoked sheet No. 1 at 50° C over calcium chloride for seven days, followed by six days' storage under tropical conditions, and this was compared with the remaining portion of the blended sample kept in the laboratory throughout the storage period. Such a comparison is not strictly the same as between a fresh rubber and one which had been stored for a long period during transit from producer to consumer, since slow changes other than those associated with drying may take place, and these in all probability contribute to the final characteristics of the rubber. However, from the point of view of investigating effects due to hardness changes on drying, the treatment given seemed likely to establish whether any major technological changes could be attributed to this source.

Comparison of relative rates of breakdown were made by subjecting 50-gram portions to twenty-five straight-through passes on a cold laboratory mill at friction ratio, and tight nip, with rolling and up-ending between each pass.

Results given in Table VI indicate that the rate of breakdown of the hardened rubber, measured by change in Mooney viscosity, is greater than for the normal fresh material, but that after a similar breakdown schedule the latter is still appreciably softer.

This effect is further confirmed when examining behavior during compounding in the A.C.S No. 1 pure-gum test mix. After a two-and-a-half-minute mixing schedule on a laboratory mill, the normal rubber gave a compound viscosity of 42 Mooney units, while for a similar schedule the hardened rubber gave a compound viscosity of 56 Mooney units. Increase of mixing time to four minutes gave a compound viscosity of 44.5 units for the latter material.

Comparisons of vulcanized properties of the fresh rubber, and of the hardened rubber at the two levels of breakdown described above are set out in Table VII.

TABLE VII

Rubber	Raw Mooney viscosity	Mixing cycle (min.)	Compound Mooney viscosity	Press-cured at 140° C											
				Tensile strength (kg./sq. cm.)			Elongation at break			Modulus at 600% (M.C.)(kg./sq. cm.)			Resilience at 70° C		
				20′	40′	80′	20′	40′	80′	20′	40′	80′	20′	40′	80′
Laboratory-stored	74	2½	42	92	120	121	870%	870%	873%	29	37	37	69.3%	73.6%	72.6%
Stored over		2½	56	124	132	116	851%	836%	820%	44	51	48	72.6%	76.8%	74.2%
calcium chloride	103	4	44½	119	313	129	887%	866%	860%	34	42	41	73.2%	74.9%	75.7%

It is evident that even after the additional breakdown required to bring the compound stock viscosity of the dried rubber close to that of the control, the former shows an improvement in general technological properties for a pure-gum mix, and it seems evident that the structure built up during drying persists after breakdown and compounding. It is unlikely, however, that improvements of this order, which are associated with hardness changes close to the maximum obtainable during drying, will prove of much practical significance to the manufacturer.

EFFECT OF DRYING CONDITIONS DURING PREPARATION

The dependence of the level of the Mooney viscosity of natural rubber on the extent of drying during storage suggested that variation in the time and conditions of sheet drying during preparation could result in different hardness levels for fresh rubber prepared from the same latex source.

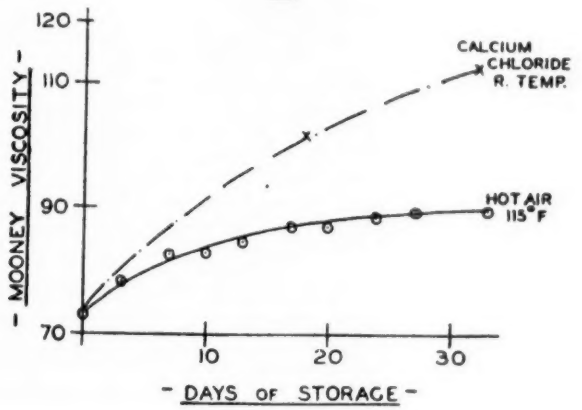
TABLE VIII

Period of drying (days)	Mooney viscosity	
	Smoked sheet	Air-dried sheet
3	Not dry	73
4	70	76½
5	71	77½
6	70	78½
7	71	78½

To confirm this, smoked sheets and air-dried sheets were prepared by normal estate factory procedures from the same bulk of latex. In each case samples were taken for Mooney testing as soon as the rubber appeared dry, judged by the production of a translucent sheet, and, in addition, sampling was carried out at intervals during continued drying.

Results are given in Table VIII, from which it is evident that increasing the drying time in the smokehouse had no appreciable effect on the level of Mooney viscosity, presumably because both Mooney and moisture equilibrium had been reached by the time the sheet appears translucent. With the hot air-dried material, however, the rubber became translucent before arrival at equilibrium

VII



with respect to Mooney viscosity and moisture content, and, consequently, increased drying time resulted in an increase in Mooney viscosity.

After removal from the estate factory drying sheds, continued drying of these samples was carried out in a laboratory hot-air chamber at 115° F, and also over calcium chloride at room temperature. All samples exhibited very similar behavior and Figure 7 illustrates a typical set of results.

Continued drying under different conditions of temperature and humidity results in a new and higher level of viscosity; in this particular experiment the values after prolonged drying at 115° F were still considerably lower than corresponding values for storage over calcium chloride.

CONCLUSIONS AND DISCUSSION

The main conclusions reached as a result of the investigations reported above may be summarized as follows:

(1) The relative humidity of the surrounding atmosphere has a marked influence on the increase in hardness of natural rubber during storage. Both raw and masticated rubbers behave in a similar manner in this respect.

(2) Increases in Mooney viscosity continue for a considerable time after the rubber has reached constant weight during drying.

(3) At a fixed temperature, the highest Mooney viscosity value is reached at the lowest relative humidity, and, in addition, the time taken to reach this value is shorter, the lower the humidity.

(4) Increases are most marked in the region below about 30 per cent relative humidity. At zero humidity, the rate of change and in all probability the extent of the increase are greater, the higher the temperature in the range examined (30° to 70° C). However, during storage in dry air oxidative breakdown becomes excessive and masks the hardening effect when temperatures are increased and storage is prolonged.

(5) The hardening is only partially reversed by subsequent storage at high humidity. At room temperature the changes are unaffected by the absence of oxygen or by the removal of acetone-soluble and nitrogenous nonrubber components and are evidently associated with the rubber hydrocarbon itself.

(6) Evidence of the formation of a benzene-insoluble gel and the development of abnormally high Williams recovery values suggest the build-up of a cross-linked structure throughout the rubber.

(7) This structure influences the breakdown characteristics of the raw rubber during mastication, and shows up in the slightly improved technical properties of vulcanized pure-gum products, persisting even after additional breakdown has been given to arrive at normal levels of compound stock viscosity.

(8) Changes in the conditions of sheet drying in an estate factory can result in different raw Mooney viscosity values for freshly prepared rubber from the same latex source. Heterogeneous humidity conditions within commercial smokehouses and drying sheds and different conditions from day to day may well account for a proportion of the variability in hardness observed with raw natural rubber.

The work described above was carried out to obtain information on storage changes, and the results are recorded primarily to cover this particular requirement. However, it is of interest to consider briefly the possible mechanisms which may be involved in the phenomena observed.

The evidence points to rubber hydrocarbon as the main participant, and

over a wide range of initial molecular weights the effects were very similar.

The hardening which takes place as a result of drying appears to be due to an increase in the number of molecular linkages present. Development of high recovery and the formation of a macrogel structure suggests that these are cross-links between chains rather than a coupling of existing units to produce longer or more highly-branched molecules.

In this connection Medalia and Kolthoff[7] have recently reported a method for the conversion of microgel to macrogel in GR-S, which involves heating in a vacuum oven at 80° C under a pressure of 20 to 40 mm. of mercury for twelve hours. Since drying-out must occur under these conditions the changes with GR-S may be closely related to those observed in the present work with natural rubber.

Probably the overall effects are the result of two opposed processes, one normal oxidative breakdown, and the other a molecular build-up which may be initiated and maintained by the presence in the fresh rubber of peroxide or similar free radical forming groups.

Under conditions of tropical storage at high relative humidity, the balance for a freshly-prepared rubber is very slightly in favor of structure build-up and a slow increase in hardness takes place until equilibrium is reached. Removal of water during storage at lower humidities upsets the balance between the opposed processes to give increased structure build-up, and the new equilibrium position is to a large extent maintained when storage is continued after return to conditions of tropical humidity.

Recent observations which still await confirmation indicate that addition to rubber of mercaptobenzothiazole or xylenethiol considerably reduces the hardening during storage in dry air. Substances of this type increase the effect of oxidative breakdown during the mastication of rubber, and may react in a similar manner in this instance.

The effect of water in shifting the equilibrium between build-up and breakdown could be accounted for in one of two ways—either as an accelerator of oxidiative breakdown or as a retarder of molecular build-up. The answer to the question as to which of these roles predominates should provide valuable insight into the nature of these changes, and may well indicate the steps which can be taken to control them.

SUMMARY

In the course of investigations carried out in connection with the technical classification of natural rubber, large permanent increases in Mooney viscosity of the order of 30 to 40 units have been observed when freshly prepared raw or masticated rubber is stored under conditions of low relative humidity.

The rate of change and the extent of the increase are both affected by the relative humidity of storage, the effects being most marked in the region below about 30 per cent relative humidity. Rate of change in dry air increases with decreasing sample thickness and with increasing temperature, although the effects are masked somewhat by oxidative breakdown on prolonged storage at temperatures higher than about 30° C.

Mooney values continue to increase long after the rubber has reached constant weight on drying; the removal of acetone soluble and nitrogenous non-rubber components and of oxygen does not prevent the changes taking place. The effects are only partially reversed by subsequent storage at high relative humidity, and there is evidence to suggest that the hardening is associated with

the development of a cross-linked benzene-insoluble gel structure throughout the rubber.

The rate of mill-breakdown of dry stored rubber is greater than for fresh rubber, but in comparisons using a fixed breakdown procedure, the hardened rubber still has a higher Mooney value after mastication. Rubbers hardened by dry air storage exhibit slightly improved vulcanized properties in a pure-gum mix even after the additional breakdown required to reach normal stock viscosity levels.

Fluctuation of temperature and humidity in commercial smokehouses and drying sheds may well account for part of the variability of natural rubber as measured by Mooney viscosity determinations on the freshly prepared product, and different conditions of storage will add a further contribution to the total hardness variation experienced by the consumer.

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The author particularly desires to record his appreciation to W. G. Wren, Acting Head of the Chemical Division of the Rubber Research Institute of Malaya, for his interest and valuable assistance throughout these investigations.

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CRYSTALLIZATION AND TENSILE STRENGTH OF VULCANIZED NATURAL RUBBER COMPOUNDS *

S. H. Morrell and Jan Stern

INTRODUCTION

It is generally accepted that the tensile strength of rubberlike materials depends critically on crystallization. Flory's[1] investigation of the influence of the molecular weight of raw rubber on the tensile strength of the vulcanizate and the work of Gee[2] and of Flory, Rabjohn and Shaffer[3] on the relation between the degree of cross-linking and the tensile strength yielded results which could be satisfactorily interpreted on this basis. However, while several authors have given estimates of the degree of crystallization in stretched rubber[4] it appears that the relation between crystallinity, cross-linking, and tensile strength has not hitherto been investigated systematically. The present paper has for its subject a study of this relation for a series of natural rubber compounds vulcanized with *tert.*-butyl peroxide. Peroxide-cured rubbers are highly suitable for physical measurements; they are probably C—C cross-linked and may thus be presumed to contain a minimum of structural irregularities. They are sufficiently transparent for flaws to be detected by inspection and are free from solid ingredients which are known to give rise to vacuoles[5] and comparatively large volume changes on stretching. This last fact is of special importance in the present investigation, where a measure of the degree of crystallization was obtained from measurements of the change of volume. The degree of cross-linking was estimated from observations of the equilibrium swelling of the compounds in benzene.

EXPERIMENTAL

MATERIALS

Best quality pale crepe or smooth smoked sheet was used in all experiments. The intrinsic viscosities $[\eta]$ of the rubbers in benzene solution fell in the range 5.3–5.5. This probably corresponds to a molecular weight range[6] of 1,000,000–1,200,000. The *tert.*-butyl peroxide was a commercial sample purified by washing with alkali, drying over sodium sulfate, and distilling under reduced pressure. A.R. benzene was used in all swelling measurements.

The compounds were vulcanized *in vacuo* by a method similar to that of Farmer and Moore[7]. For the crystallization experiments, small rings (volume about 0.1 c.c., i.d. 1 cm.) were cut from pale crepe which had been cast into sheets, using a standard mold and heating for 15 minutes at 130° C. About twelve of these rings were fitted over a uniform glass tube (o.d. 1 cm.), leaving at least $\frac{1}{8}$-inch gaps between rings, and placed in a Carius tube. The Carius tube was drawn out, connected to a vacuum line, and the system evacuated for 30 minutes. An amount of peroxide, varying from 2 to 8 per cent on the volume of rubber, was next added from a pipette. The Carius tube was protected with

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a calcium chloride tube and frozen in liquid air before being reconnected to the vacuum line. After degassing the tube in the usual way by alternate freezing, pumping, and melting, the system was evacuated to 10^{-5} mm. with the peroxide frozen, and the Carius tube sealed. The rubber and peroxide were allowed to equilibrate for at least 48 hours and then cured for 6 hours at 140° C. The *tert.*-butyl alcohol formed in the reaction was pumped off. For the tensile measurements, pieces of smooth sheet were similarly vulcanized at 140° C, varying the amount of peroxide and the time of cure. Standard dumb-bell test-pieces were cut from the vulcanizate. A few crystallization experiments were also made with lightly degraded samples: the rubber was milled to a Mooney viscosity of about 60, corresponding to $[\eta] \simeq 2.8$ and a molecular weight of about 500,000. The peroxide (1.5–2 per cent) was added on the mill and the mix cured in the form of $6 \times 6 \times \frac{1}{8}$-inch sheets at 160° C. The time of cure varied between 8 minutes and an hour, no precautions being taken to exclude oxygen. Rings for the measurements were then cut from the cured sheet.

MEASUREMENTS OF THE VOLUME CHANGES

The volume changes were measured by the method of hydrostatic weighing. The frame used, which has been described elsewhere[5], carried eight rings, which could be stretched in pairs to elongations[8] ranging from 40–570 per cent. Measurements were made as follows. The frame and the unstretched rings were immersed in water and their combined weight was observed on an automatic analytical balance over a period of about fifteen minutes, until frame and rings had reached equilibrium with the bath. The rings were then stretched and the weight was observed for 6–8 minutes, after which the rings were released and the weight again observed for several minutes. The volume change on crystallization was calculated from the difference in weight of the stretched and unstretched states. Four values of the volume change were obtained for each elongation.

If the volume changes are to be related quantitatively to the degree of crystallization, it is necessary to show that there are no spurious volume changes caused by vacuoles formed about solid impurities, or flaws when the rubber is stretched. The absence of such vacuoles was shown by observing the volume changes on stretching at elongations of 40, 115, and 200 per cent, *i.e.*, below the crystallization point. Owing to the small volume of rubber used the expansion could not be measured at these low elongations, but was less than the sensitivity of the method (about 0.01 per cent) in all cases at 40 per cent and at 115 per cent, and less than 0.025 per cent at 200 per cent. The expansion calculated from the stress-strain curve and the compressibility of rubber[5] is of the order of $\sim$0.01 at 100 per cent elongation and $\sim$0.02 per cent at 200 per cent elongation for the type of compound used in the experiments.

The quantitative aspects of the results are also affected by irreversible changes in the rubber, such as stress relaxation and permanent set. An estimate of these was obtained by measuring the internal diameter of the rings with a travelling microscope some weeks after the completion of the experiments. This proved difficult, since the edges of the rings were not very well defined, and permanent set alters the shape as well as the size of the rings. However, in no case was there a change in the diameter greater than 2 per cent, and this factor was, therefore, neglected in calculating the elongations.

Variations in the temperature effect the degree of crystallization and thus affect the results. Goppel[9] found that, at 17° C, and for an elongation of 460

per cent, the degree of crystallization changed by about 1 per cent per degree. The present experiments were made in an insulated room in which the temperature change in the course of an afternoon was less than 1° C, and the drift during the determination of a volume-elongation curve usually considerably less. All volume-elongation curves were determined in the temperature range $16.5 \pm 2°$ C.

An additional source of error is the effect of the variations in temperature on the volume of the rubber, but it follows from the consistency of the readings for the unstretched rubber that these factors do not interfere with the measurements.

The most troublesome feature of the crystallization experiments was the time-dependence of the degree of crystallization. Holt and McPherson[10] found that the volume of stretched rubber continued to change for months without apparently reaching equilibrium. Similar observations were made by Flory[11]. The rate of stretching is of secondary importance[12]. In the present experiments the final reading was taken after 6–8 minutes: the short interval was chosen in order to make the conditions compare more nearly with those obtaining in tensile tests. It is doubtful if true thermodynamic equilibrium is attainable when rubber is allowed to crystallize on stretching, and in any case, undue prolongation of the experiments was clearly undesirable for practical reasons. The procedure adopted was thus a compromise, made with the object of achieving equilibrium with respect only to the rapidly changing parameters. In practice, after 8 minutes there were no further volume changes within the sensitivity of the method at elongations above 350 per cent, and at elongations up to 200 per cent the volume did not change after the first reading. At intermediate elongations there were indications that, whereas the major portion of the density change had doubtless occurred, the volume was still changing at a rate just detectable on the balance (viz., 0.01 per cent over 1–2 minutes).

MEASUREMENT OF THE DEGREE OF CROSS-LINKING

For the swelling measurements, a weighed sample of the rubber (about 0.5 gram) was immersed in benzene in a tube provided with a ground-glass stopper. The tube was swept out with nitrogen and kept in a thermostat at 25° C. After 4-5 days the samples were taken out, surface dried, and weighed. In all cases the samples were reweighed after swelling for a further day, and the invariable result was that the volume of benzene absorbed was reproducible to a greater extent than 1 per cent. From the ratio of the volumes of benzene and rubber, Qm, the molecular weight between cross-links, M_c, was calculated from the equation[13]:

$$\ln\left(1 + \frac{1}{Qm}\right) - (Qm + 1)^{-1} = \mu(Q_m + 1)^{-2} + \frac{\rho_r V_0}{M_c}(Q_m + 1)^{-1} \qquad (1)$$

The value taken for μ, the interaction constant of the system rubber-benzene,[2] was 0.39_5 the densities of rubber, ρ_r, and benzene (required for the calculation of the molar volume of benzene, V_0) were determined as 0.917 and 0.873 at 25° C. All M_c values were corrected for soluble substances in the rubber.

MEASUREMENT OF TENSILE STRENGTH

Tensile-strength measurements were carried out on a conventional Goodbrand testing machine, using standard dumb-bell test-pieces, since it was found

impossible to measure satisfactorily the tensile strengths of the rings used in the experiments. Unless otherwise stated, the tensile strengths refer to the cross-section at break.

RESULTS AND DISCUSSION

Volume-extension curves for the compounds investigated are given in Figure 1. In Figure 2 the change of volume is plotted against the degree of cross-linking for several elongations. Figure 3 shows a graph of the tensile strength and ultimate elongation against the degree of cross-linking, and Figure 4 relates the extrapolated volume change at break to the degree of cross-linking.

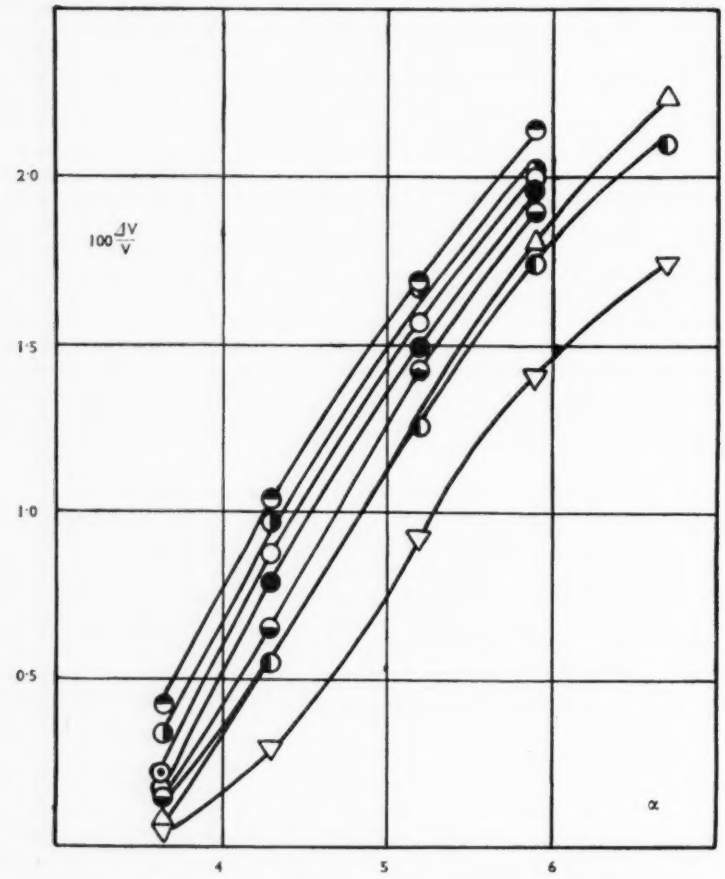

FIG. I.—Volume-elongation curves for peroxide cured rubber samples.

Tube cures:

(*a*) ◐ $10^4/M_c = 0.893$ (*d*) ○ $10^4/M_c = 1.299$
(*b*) ◒ $10^4/M_c = 1.031$ (*e*) ◓ $10^4/M_c = 1.639$
(*c*) ● $10^4/M_c = 1.163$ (*f*) ◑ $10^4/M_c = 1.786$

Press cures:

(*g*) ▽ $10^4/M_c = 1.020$ (*h*) △ $10^4/M_c = 1.429$

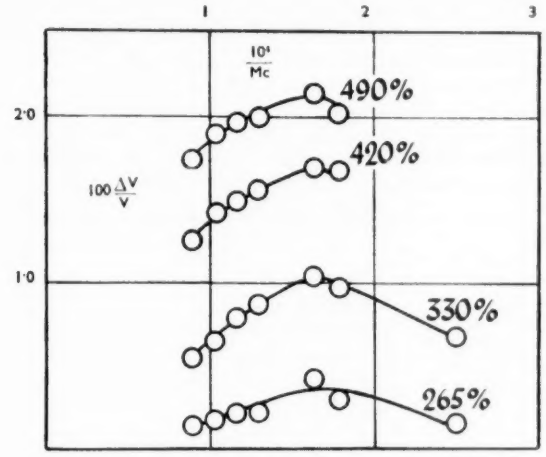

FIG. 2.—Dependence of volume change on cross-linking at 265 per cent, 330 per cent, 420 per cent and 490 per cent extension.

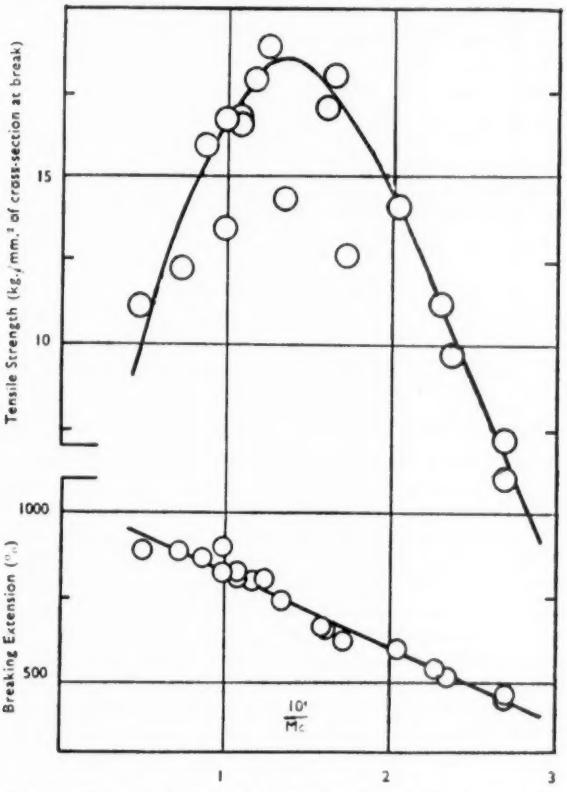

FIG. 3.—Effect of cross linking on tensile strength and ultimate elongation.

Recently, Flory, Rabjohn and Shaffer[3] have suggested that M_c-values calculated from Equation 1 are erroneous, especially for lightly cross-linked rubbers. Any such errors should, however, only affect the absolute values of M_c without invalidating the discussion which follows.

From Figures 1 and 2 it will be seen that the volume changes first increase and then decrease with increasing degree of cross-linking, but the effect is not very large, especially at higher elongations. Initially, at any given elongation, a greater number of cross-links causes greater alignment of the chains, sup-

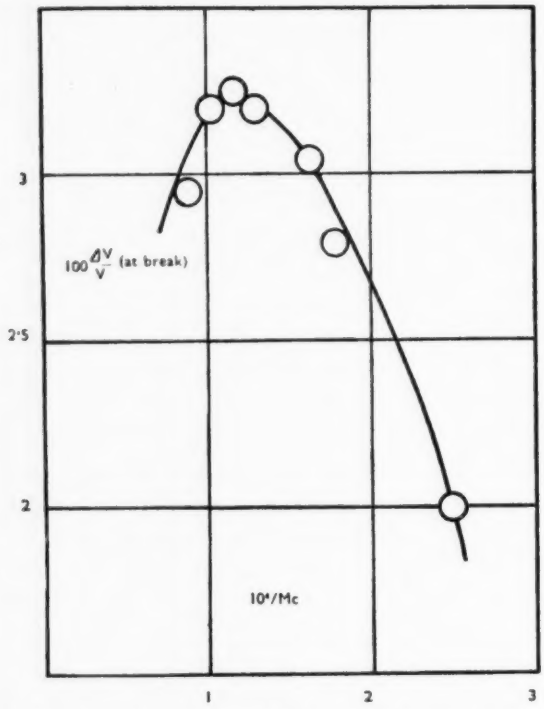

FIG. 4.—Relation between cross-linking and the (extrapolated) volume change at break.

presses flow and leads to higher degrees of crystallization. Beyond a certain degree of cross-linking, progressively greater portions of the chain are incapable of taking part in crystallization; this finally leads to a decrease in the degree of crystallization with cross-linking. We have also to consider other factors which may be responsible for the lower crystallinity of the highly cross-linked samples. First, it is a well-known fact that the rate of crystallization of unstretched rubber decreases sharply with cross-linking. Observations of the rate of change of volume indicate that this factor is probably unimportant in the present experiment. Second, chemical interaction other than cross-linking may take place between the rubber and peroxide, leading to chain scission, a reduction in the proportion of active network chains, and thence of the degree of crystallization. That this factor is very important for lightly cross-linked compounds cured in the presence of oxygen can be seen from the data for press-

cured samples included in Figure 1. The effect is very great for the sample of $10^4/M_c = 1.02$ (g), and much less for the more highly cross-linked sample of $10^4/M_c = 1.43$ (h). The reduction of the degree of crystallization is presumably due partly to the lower primary molecular weight of these compounds, and partly to further degradation due to the presence of oxygen during the cure. In the case of the vacuum cures, care was taken to exclude oxygen. Whereas the possibility of slight degradation of the samples cannot of course be definitely excluded, no evidence for this was found, and its effect must have been very small. It was found impossible to prepare suitable vacuum-cured samples of high degrees of cross linking. Highly cross-linked peroxide compounds were prone to tear (when stretched on the frame), and they frequently broke at elongations well below those found in the usual tensile test before the volume change could be measured. After many attempts, data were obtained for a press-cured sample of $10^4/M_c = 2.5$ at two elongations, and these are included in Figures 2 and 4. We believe that the effects of degradation and lower primary molecular weight are small at the high degree of cross-linking of this sample, and that, although the values of $\Delta V/V$ are not strictly comparable, the error involved in their use is small.

Finally, a factor difficult to assess is the magnitude of the expansion due to the hydrostatic component of the applied force[5]. The magnitude of this expansion cannot be predicted[14], but it must be greater for the more highly cross-linked (high modulus) compounds. Rough calculations on the lines of those described[5] show that the effect would certainly be important, possibly up to 0.1 per cent of the original volume at 400 per cent elongation; there are, however, grounds for believing[14], that in the region of high extensions when the rubber is no longer isotropic, the expansion is less than that calculated from theory. Nevertheless, this uncertainty is one of the major hindrances to the precise determination of the degree of crystallization by measurement of the volume change. However, it is considered that the difference in the magnitude of the effect for the lightly and highly cross-linked samples is not sufficient to affect materially the general shape of the crystallization curves, which are believed to be substantially correct.

The shape of the tensile strength $\sim$ cross-linking curve and the position of the maximum in the tensile strength are in reasonable agreement with the result of previous investigations, but the tensile strengths throughout are lower than those found by Gee[2].

An attempt was made to correlate tensile strength with crystallization at break. For this purpose it was necessary to extrapolate the volume-extension curves a considerable way, and the uncertainty in the value of that break is correspondingly large. Consequently the relation between $\Delta V/V$ at break and $10^4/M_c$ could not be determined with any great precision. The results are shown in Figure 4, where it is seen that the curve of $\Delta V/V$ at break is similar in shape to the tensile strength curve, and the maxima occur roughly in the same region, showing the close interdependence of these quantities. The lower crystallization at break and tensile strength of the lightly cross-linked samples ($10^4/M_c < 1$) can at least in part be attributed to the lower slope of the $\Delta V/V \sim \alpha$ curves and the necessary higher elongation for incipient crystallization of these compounds. In addition, flow phenomena, which tend to reduce both crystallization and tensile strength, must become increasingly important as the degree of cross-linking is reduced.

The main cause of the decrease in the crystallization at break and tensile strength at high degrees of cross-linking, on the other hand, must be sought in

the high modulus of highly cross-linked samples, which leads to high loads and rupture at low elongations before the material has become sufficiently strengthened by crystallization[2]. The tensile strength and crystallization at break are further diminished by the decrease of crystallization at high degrees of cross-linking.

Experimental data indicate that compounds breaking at elongations below about 350 per cent must do so without crystallizing to any appreciable extent. Figure 3 shows that such compounds, like many noncrystalline polymers, are very weak (tensile strength about 1 kg. per sq. mm.).

In conclusion, it should be pointed out that, although it is possible to explain the general tensile behavior of the peroxide-cured samples satisfactorily in terms of crystallization, other factors, chemical and physical, must affect the tensile strength of rubber. This is clear from the work of Gee[2], who found tensile strengths nearly 100 per cent higher for boosted sulfur cures (containing 5 per cent ZnO) over a comparable range of cross-linking.

SUMMARY

The effect which changes in the degree of cross-linking have on the crystallization of stretched rubber has been studied by observing the densities of a series of peroxide-cured natural rubber compounds. It was found that at any one elongation, crystallization first increased and then decreased with increase in the degree of cross-linking. The significance of this maximum and the relation between crystallization and tensile strength are discussed.

ACKNOWLEDGMENT

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$$\alpha = 0.5\ [\alpha_r + (1 + r_1 r_2)^{-1}\ (\alpha_r^{\frac{1}{2}} - 1))^{\frac{1}{2}}]$$

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PHYSICAL ASPECTS OF GR-S AND ALFIN POLYMER MODIFICATIONS *

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PHYSICAL ASPECTS

The molecular structure of natural and synthetic rubbers has been the subject of lively discussion and the basis of much experimental work in recent years. Research in this field has been particularly fruitful with the development of new chemical and physical tools for grappling with this complicated problem.

A research project of particular interest is Bloomfield's recent work on the composition of natural rubber as it occurs in the tree[1]. The finding that the rubber hydrocarbon in the tree is of significantly higher molecular weight than was previously thought to be the case is of particular interest in this discussion. We shall discuss GR-S modifications of substantially higher molecular weight than the standard polymers available until recently in the synthetic rubber program. Bloomfield's discovery of microgel in natural-rubber latex, and the anomalous relation between plasticity and intrinsic viscosity when cross-linked polymer is present, are also of interest, since comparable results have been obtained with GR-S synthetic rubbers of high molecular weight.

It has now become clear that exact duplication by man of the macro- and microstructure which natural rubber possesses cannot be accomplished in the foreseeable future. The preponderance of available data suggests that natural rubber possesses a remarkably uniform molecular structure, in which the isoprene units are joined by 1,4-addition in a regular head-to-tail fashion, and with the *cis*-configuration around each of the double bonds. Such a regular structure permits a high percentage of the molecules to array themselves into a crystalline pattern when stretched, and, thus internally reinforced, to exhibit high tensile strength in unfilled stocks. Such behavior cannot be matched by synthetic butadiene or isoprene polymers, although some cold rubbers, when tested as latex-cast films, have shown considerable improvement in tension strength over regular GR-S.

GR-S and Buna-S are basically similar polymers except in molecular weight and molecular-weight distribution. GR-S as ordinarily produced is a completely benzene-soluble polymer, with a Mooney viscosity of 50 ML-4, and a dilute solution viscosity of 1.8 to 2.0. It exhibits a rather broad molecular-weight distribution, from soft gummy material to very tough nervy rubber polymer. The molecular weight varies from a few thousand to over a million, with a large fraction of the weight of the polymer in the range of 100,000 to 300,000.

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* Reprinted from a paper in the *Transactions of the Institution of the Rubber Industry*, Vol. 28, No. 4, pages 166–206, August 1952. This reprinting includes practically all of the original paper except the opening general introduction and discussion of the economics of natural and synthetic rubber at the present time. Because of this omission, the original title, "Economics and Physical Aspects of GR-S Modifications," has been changed, by suggestion of the author, to "Physical Aspects of GR-S and Alfin Modifications." The paper is the printed version of the seventh Foundation Lecture of the Institution of the Rubber Industry, delivered by R. P. Dinsmore at Wolverhampton, England, May 23, 1952.

Buna-S, on the other hand, is of much higher average molecular weight, contains very little of the soft gummy material in GR-S, but does have a substantial amount of gel. It is prepared in a polymerization recipe containing little modifier. The original Buna-S was produced with a soap of linseed oil as the emulsifier, which also acted as a mild chain transfer agent. It had a plasticity corresponding to a Defo number of 5000 (Defo 500 is approximately 50 ML-4, Defo 5000 is over 200 ML-4). Later, production was shifted to Buna-S3, with a Defo value of 3000, made in a recipe containing paraffin fatty acid soaps and Nekal (sodium diisobutylnaphthalene sulfonate) as emulsifiers, and a small amount of diisopropylxanthic disulfide as chain-transfer agent. The Bunas are of such high molecular weight that they must be heat-softened to be usable on conventional rubber processing equipment. After heat softening, the average molecular weight is greatly decreased and the gel content disappears, so that the molecular weight distribution more closely approximates that of GR-S, with the exception of a larger proportion of the high molecular-weight fractions.[2]

It is questionable whether any significant differences in microstructure exist in GR-S and Buna-S. They are made at approximately the same temperature (40–50° C) to approximately the same conversion (60–72 per cent) and styrene content (20–25 per cent). Such differences of properties as exist must be attributed almost entirely to differences in the macrostructural features just described.

Lowered polymerization temperature, however, is now definitely known to produce profound differences in both micro- and macrostructural features. Let us compare GR-S polymerized at 50° C with cold rubber produced at 5° C.

One of the first changes noted is the more regular combination of butadiene and styrene. At 50° C a striking heterogeneity exists with respect to the butadiene-styrene ratio of copolymer formed at various conversions.[3] For example, a 78 per cent conversion GR-S with an average styrene content of 21.0 per cent is actually made up of polymer units containing from 17.2 to 28.6 per cent styrene. Much less variation exists when the polymerization is conducted at lower temperatures[2].

Substantially less modifier is required at lower temperatures to produce 50 ML polymers than at 50° C. Molecular-weight distribution studies indicate less low molecular-weight fraction and more high molecular-weight fraction in cold rubber than in regular GR-S. Comparison of intrinsic viscosity data and average molecular weight for polymers prepared at various temperatures definitely indicates a more regular structure (less cross-linking) with lowered polymerization temperatures.[4]

Lower polymerization temperature exerts a negligible effect on the proportion of 1,2- and 1,4-addition of butadiene. About 23 per cent of the butadiene polymerized at 50° C enters the polymer by 1,2 addition; this value drops about 3 to 4 per cent when the polymerization temperature drops to −20° C. Of greater interest, however, is the effect of temperature on the *cis*- and *trans*-configurations around the double bonds formed by 1,4-addition of butadiene[2]. In polymers prepared at 50° C, about 75 to 80 per cent of the internal double bonds formed by 1,4- addition exhibit the *trans*-configuration. At 0° C, this value is over 90 per cent, and at −20° C polymerization temperature virtually all the internal double bonds exhibit the *trans*-configuration. These conclusions from infrared absorption studies are substantially confirmed by *x*-ray studies of structural regularity in butadiene polymers prepared at various temperatures[5], and by dilatometer studies of crystallization and regularity[6].

In brief, cold rubber differs from GR-S by possessing a more regular structure. Internally, the molecules are more homogeneous with respect to distribution of styrene content in individual molecules, and with respect to geometric configuration around the internal double bonds. There is less of the very low molecular-weight fraction, so the overall molecular-weight distribution is somewhat narrower than for GR-S; in other words, the average molecular weight of cold rubber is substantially higher than for GR-S. The amount of cross-linking and branching is also considerably reduced. These factors are favorable, since they are conducive to more complete and efficient reaction of the polymer with carbon black, and thus result in higher tensile strength, tear strength, flex life, and abrasion resistance. The result is improved quality in the final product.

The enhanced demand for natural and synthetic rubbers during the past two years has prompted rubber chemists to reconsider a number of possibilities for extending the supplies of available materials, preferably with no sacrifice in quality of the finished product. This search has led to the development of oil-masterbatched synthetic rubbers, which have recently been described in some detail[7]. The work described in this paper was started privately and was later incorporated into a comprehensive program sponsored by the Reconstruction Finance Corporation for the United States Government. An excellent summary of the literature on oil-rubber blends was prepared by Rostler[8].

From this work has arisen confirmation of the fact that polymers of very high molecular weight possess intrinsically superior quality, particularly with respect to resilience properties. They can tolerate dilution or extension with substantial amounts of inert materials, such as conventional rubber processing oils, and thereby form masterbatches which retain the good properties of the base polymer. The oil apparently functions as an "internal lubricant" and thus allows polymers to be processed in conventional equipment, which otherwise would not be suitable.

There is some question as to the effect of gel content in the base polymer. Results obtained to date indicate that high contents of gel, particularly of tightly netted structure, *i.e.*, low swelling index or grams of benzene held by 1 gram of gel, are detrimental from the standpoint of both physical properties and processing characteristics. Early experience with GR-S indicated that presence of gel was undesirable, and present experience with oil-masterbatches tends to confirm this point. The presence of oil is beneficial from this standpoint, as it tends to prevent the formation of gel, or solubilizes gel already formed, providing it is not too tightly cross-linked. The chemical composition of the oil is also important; oils of greater solvation power, *i.e.*, high aromatic hydrocarbon content, are more effective than those of lesser solvation power.

It is our purpose to describe some of our recent work on the preparation and properties of oil-rubber masterbatches, including data on their performance in extensive tire tests.

LABORATORY STUDIES OF PREPARATION OF OIL–RUBBER MASTERBATCHES

To gain background information for subsequent large-scale operations, a systematic study was made of polymerization variables involved in the preparation of high molecular-weight cold GR-S suitable for oil-masterbatching studies. Polymers were prepared in 4-oz. bottles at 50° F to 60 per cent and 90 per cent conversion, employing a wide range of modifier content, and latex-masterbatched with different amounts of oil.

A typical sugar-free cold-rubber formulation was used:

Butadiene	75
Styrene	25
Water	200
Sodium fatty acid soap	2.0
Dresinate 214[a]	2.0
$Na_3PO_4 \cdot 12H_2O$	0.30
Tamol-N[b]	0.15
$FeSO_4 \cdot 7H_2O$	0.154
$K_4P_2O_7$	0.172
Sulfole[c]	Variable
Conversion	60, 90%
Shortstop { 0.10 sodium dimethyldithiocarbamate; 0.05 tetraethylene pentamine	
Antioxidant 1.25 per cent PBNA (phenyl β-naphthylamine).	

[a] Potassium soap of disproportionated rosin acid (Hercules Powder Co.).
[b] Sodium salt of condensed alkylaryl sulphonic acid (Rohm & Haas Co.).
[c] *Tert.* C_{12} thiol (Phillips Petroleum Co.).

The Sulfole modifier concentration was varied from zero to 0.15 part, and conversion was carried to 60 per cent in $2\frac{3}{4}$ hours and to 90 per cent in 6 hours. The rates of polymerization were such that latexes could be made, shortstopped, stripped, oil-masterbatched, and coagulated on the same day. The oil (Circo-

TABLE I

CHARACTERIZATION OF LABORATORY OIL–POLYMER MASTERBATCHES
(Bottle Scale—Series 2023–2065)

Apparent gel content (%)—based on contained polymer

Parts Circosol-2XH (on polymer)	60 per cent conversion—Sulfole (parts)					90 per cent conversion—Sulfole (parts)				
	0.15	0.10	0.05	0.025	None	0.15	0.10	0.05	0.025	None
0	10	27	43	80	83	56	77	80	82	91
10	6	—	—	—	—	60	—	—	—	—
25	3	13	23	—	—	49	69	76	—	—
50	17	17	36	56	71	46	64	69	69	75
75	—	0	40	39	67	—	30	40	47	72
100	—	—	—	32	40	—	—	—	32	64

Swelling index (g. benzene held by 1 g. polymer gel)

Parts Circosol-2XH (on polymer)	60 per cent conversion—Sulfole (parts)					90 per cent conversion—Sulfole (parts)				
	0.15	0.10	0.05	0.025	None	0.15	0.10	0.05	0.025	None
0	88	87	82	39	37	88	43	33	34	21
10	275	—	—	—	—	71	—	—	—	—
25	—	78	132	—	—	97	49	38	—	—
50	38	38	66	75	47	100	66	50	48	40
75	—	—	38	94	43	—	108	87	83	31
100	—	—	—	71	48	—	—	—	158	48

D.S.V. of soluble portion

Parts Circosol-2XH (on polymer)	60 per cent conversion—Sulfole (parts)					90 per cent conversion—Sulfole (parts)				
	0.15	0.10	0.05	0.025	None	0.15	0.10	0.05	0.025	None
0	3.16	3.55	2.09	2.36	1.96	1.39	1.02	0.81	0.93	0.83
10	3.08	—	—	—	—	0.85	—	—	—	—
25	2.93	3.75	3.10	—	—	1.03	0.64	0.50	—	—
50	3.33	3.94	4.14	2.47	2.37	1.07	0.63	0.37	0.70	0.19
75	—	3.31	3.99	2.38	2.47	—	1.40	0.60	0.73	0.28
100	—	—	—	2.80	2.76	—	—	—	0.70	0.39

sol-2XH) concentration was varied from 0 to 100 parts on the weight of polymer, depending on the modifier level.

The oils were added to the latexes as 50 per cent aqueous emulsions containing 2 per cent sodium oleate (calculated on the oil content). The emulsion was prepared *in situ* by dissolving oleic acid in the oil and caustic in the water. The latex masterbatches were coagulated as crumb when possible, by the addition of salt and sulfuric acid. Masterbatches containing more than 50 parts oil were difficult to dry, since most of them did not give a satisfactory crumb.

The gel contents, swelling indexes, and dilute solution viscosities in benzene were determined in the usual way, and the data are collected in Table 1. Examination of these data discloses the following general trends:

(1) The contained polymer is rendered more soluble in benzene as a result of the presence of oil; *i.e.*, the gel content of the raw polymer is higher than the apparent gel content (calculated on the contained polymer) in the oil masterbatch. This trend toward increased solubilization is accentuated with increasing concentration of oil.
(2) The gel content tends to increase with decreasing modifier concentration at all oil concentrations.
(3) The gel content is generally higher for the higher conversion at all oil and modifier concentrations.
(4) There is no trend in swelling indexes of gel polymer with polymerization variables or with gel content.

A series of three 5-gallon reactor batches was also run to obtain additional information on these polymerization variables and to furnish samples for the determination of the effect of molding conditions on modulus of the raw masterbatches. The X-628 recipe was used at 50° F, and the modifier and oil content were varied as shown in Table 2.

TABLE 2

CHARACTERIZATION OF LABORATORY OIL–POLYMER MASTERBATCHES
(5-GALLON REACTOR PREPARATIONS)
(X-628 RECIPE—60 PER CENT CONVERSION)

RXL-	Sulfole (parts)	Circosol-2XH on polymer (parts)	Gel (per cent)	Swell index	DSV	ML-4
3951	0.15	0	0	—	2.86	—
	0.15	25	0	—	2.57	59
	0.15	50	0	—	2.58	33
3952	0.10	0	0	—	3.44	—
	0.10	25	0	—	2.98	73
	0.10	37.5	0	—	2.85	58
	0.10	50	0	—	2.76	42
3942	0.05	0	42	110	2.50	—
	0.05	25	18	180	3.19	104
	0.05	50	7	—	2.62	73

The raw polymers prepared with 0.15 and 0.10 part Sulfole to 60 per cent conversion were gel-free, as, of course, were their oil masterbatches. The gel content of the raw polymer and oil masterbatches made with 0.05 Sulfole decreased as the oil was increased.

On the basis of Mooney viscosity values, it would appear that the masterbatch made with 0.15 Sulfole and containing 25 parts of oil is equivalent to one made with 0.10 Sulfole and containing 37.5 parts oil, and approximately equivalent to one made with 0.05 Sulfole and containing 50 parts of oil.

PILOT PLANT PREPARATIONS OF OIL–RUBBER MASTERBATCHES

Following preliminary laboratory scale trials, larger preparations of oil-rubber masterbatches were scheduled at the Goodyear pilot plant for large-scale evaluations. Some of the representative runs are listed in Table 3.

TABLE 3

COLD RUBBER–OIL MASTERBATCHES PREPARED BY GOODYEAR PILOT PLANT [a]

Code no.	Sulfole	Per cent conversion	MS base polymer	Oil[f] per 100 polymer	ML final	Per cent gel[b]	Swelling[c] index	DSV[d]
A	0.09	60	70	25	50	—	—	3.39
B	0.09	63	75	25	64	6	176	5.26
C	0.09	63	75	37	56	8	147	3.48
D	0.10	63.6	68	25	52, 60	11	98	2.95
E	0.10	63.6	68	25	51, 64	18	63	3.43
F	0.10	60.6	65	25	54	0	—	2.82
G	0.10	60.6	65	25	51	—	—	—
H	0.15	73.4	67	25	65	4	330	3.62
I	0.15	73.4	67	37.5	63	4	181	3.81
J	0.15	73.4	67	50	39	0	—	3.48
K	0.10	71.8	76	25	93	10	88	4.31
L	0.10	71.8	76	37.5	63	8	120	4.32
M	0.10	71.8	76	50	53	17	18	4.86
N	0.05	72	89	25	100	0	—	4.16
O	0.05	72	89	37.5	86	25	96	4.84
P	0.05	72	89	50	63	16	136	4.88
Q	0.025	72	80[e]	25	93	75	44	2.85
R	0.025	72	80[e]	37.5	82	70	50	2.87
S	0.025	72	80[e]	50	52	63	72	2.53

[a] All polymers made with butadiene/styrene charging ratio of 75/25.
[b] Calculated on weight of polymer without oil.
[c] Grams benzene held by 1 g. of gel rubber.
[d] $\text{DSV} = \frac{2.3 \log_{10} (\text{relative viscosity})}{\text{Concentration (g. polymer/100 cc. solution)}}$.
[e] Questionable values because of high gel content.
[f] Polymer E contained Shell oil L225, and polymer G contained Shell oil SPX-97. All others prepared with Circosol-2XH.

These were polymerized in a 1200-gallon glass-lined reactor in a sugar-free formulation at 41° F, with a mixed fatty-rosin acid soap emulsification similar to that described previously for laboratory studies. After the latex was short-stopped and stripped of unreacted monomers, it was in many cases split into several portions for the addition of various amounts of rubber processing oil (emulsified in sodium oleate solution).

The first polymer listed, A, is similar in all respects to X-628, the first oil-masterbatched polymer scheduled for production at Houston, Texas. The next two, B and C, were made under similar conditions but contained 25 and 37 parts of Circosol-2XH added to the same base latex. The next four, D, E,

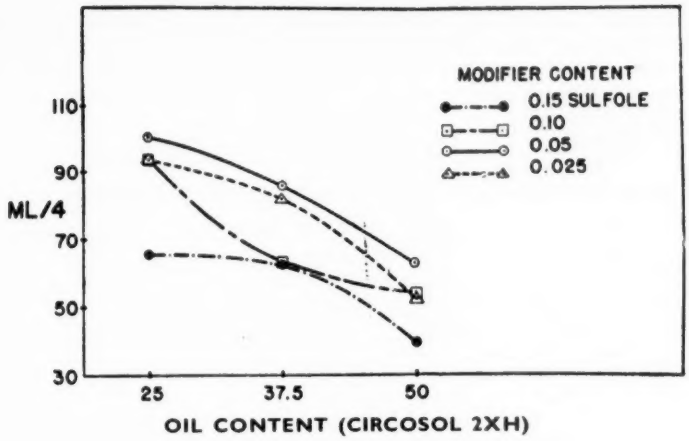

FIG. 1.—Mooney viscosity of oil-polymer master-batches.

F, and G, all contain 25 parts of oil, and include a comparison of Circosol-2XH with two other processing oils, L225 and SPX-97 (Shell Oil Co.). The next twelve, H to S, inclusive, represent a systematic variation in modifier and oil content. Four polymerizations were conducted at various levels in Sulfole modifier content (0.15, 0.10, 0.05, 0.025) to 72 per cent conversion. Each latex was then split into three portions and masterbatched with 25, 37.5, and 50 parts of Circosol-2XH.

A study of the raw polymer properties of the masterbatches in this last group is of interest. It will be noted that the Mooney viscosity of the product decreases with increasing modifier and oil content, as expected. However, the polymers made with the least amount of modifier exhibit lower Mooney viscosity values than expected. More informative data are obtained by determining dilute solution viscosity (DSV) in benzene, gel content, and swelling index of gel, of each masterbatch.

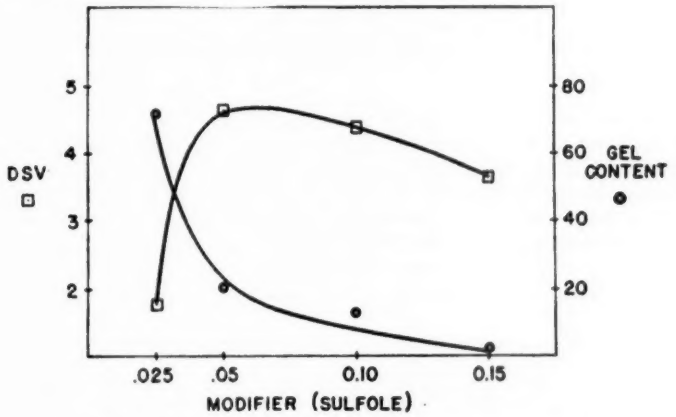

FIG. 2.—Raw polymer properties as function of modifier concentration.

Here it is noted that, with decreasing amounts of modifier, the gel content increases and its swelling volume decreases, the DSV values rise to a maximum and then fall off rapidly, with the least amount of modifier. It seems clear that the anomalous Mooney values are associated with the presence of large amounts of tight gel in the latter case. The Mooney viscosity values are plotted in Figure 1 and the DSV and gel content data in Figure 2.

MILL BREAKDOWN OF OIL–POLYMER MASTERBATCHES

A study of the effect of milling at 120° F (±10° F) for a period of thirty minutes was made on X-628 base polymers containing 0, 25, 38, and 48 parts Circosol-2XH per 100 parts of polymer.

Samples were taken every five minutes for determination of dilute solution viscosity, gel content, and swelling index (all calculations based on weight of oil-free polymer). The data are collected in Table 4. The initial gel content

TABLE 4

MILL BREAKDOWN AT 102° F OF OIL–POLYMER MASTERBATCHES

Milling time (minutes)		0	5	10	15	20	25	30
Polymer								
X-628 base	DSV	3.52	3.01	2.92	2.71	2.50	2.46	2.41
No oil	% gel	49	31					
	SI	126	63					
X-628 base	DSV	2.98	2.87	2.64	2.54	2.55	2.51	2.47
25 oil	% gel	42						
	SI	94						
X-628 base	DSV	3.65	3.13	2.86	2.80	2.67	2.61	2.56
38 oil	% gel	33						
	SI	37						
X-628 base	DSV	3.56	3.16	2.93	2.89	2.74	2.56	2.50
48 oil	% gel	36						
	SI	29						
GR-S-101 control	DSV	1.73	1.65	1.68	1.63	1.63	1.67	1.60

DSV = Dilute solution viscosity (based on concentration of oil-free polymer).
SI = Swelling index (g. benzene held by 1 g. gel rubber).

was completely solubilized in five minutes of milling the oil masterbatches; the control polymer without oil still contained 31 per cent gel after five minutes, but it also completely disappeared with ten minutes' milling. The DSV values decreased rather sharply in the first ten-minute period, then slowly declined for the rest of the test. Even at the end of thirty minutes the DSV was high, about 2.5, compared to 1.73 for standard cold rubber (unmilled). The polymers containing oil exhibited somewhat less breakdown than the oil-free control, as measured by final DSV values, but the differences were rather small.

OVEN-AGING OF OIL–POLYMER MASTERBATCHES

A study was made of the changes occurring when oil-polymer masterbatches were heated at 180° F in a circulating air oven for various periods up to 32 hours. Samples were cut in thin strips to obtain maximum and uniform ex-

posure to air and heat. Changes in the Mooney viscosity, dilute solution viscosity (DSV), gel content, and swelling index (SI) of the gel are presented in Table 5 and plotted in Figure 3.

TABLE 5

OVEN AGING AT 180° F OF OIL–POLYMER MASTERBATCHES

Aging time (hours)		0	0.5	1.0	2.0	4.0	8.0	15.0	32.0
Polymer									
X-628 base	ML-4	—	153	157	154	150	153	149	137
No oil	DSV	3.52	2.26	2.04	2.10	2.12	1.99	2.04	2.08
	% gel	49	30	32	39	36	35	31	26
	SI	126	189	172	141	144	141	174	194
X-628 base	ML-4	—	83	82	83	88	86	80	67
25 oil	DSV	2.98	2.45	2.51	2.34	2.40	2.31	2.31	2.37
	% gel	42	42	35	25	30	32	34	36
	SI	94	90	107	166	143	127	125	113
X-628 base	ML-4	68	69	67	69	65	70	67	65
38 oil	DSV	3.28	3.05	3.17	2.83	2.83	2.74	2.61	2.70
	% gel	9	15	15	20	30	38	37	30
	Si	471	441	342	341	212	174	187	260
X-628 base	ML-4	59	49	55	55	57	54	51	45
48 oil	DSV	3.04	2.96	2.76	2.75	2.58	2.80	2.72	2.77
	% gel	12	13	19	16	21	23	51	70
	SI	339	435	242	278	236	198	59	57
GR-S-101	ML-4	61	57	60	57	58	60	60	61
control	DSV	1.87	1.87	1.91	1.89	1.91	1.90	1.89	1.88
	% gel	2	—	1	2	1	1	—	1
	SI	22	—	82	35	73	60	—	45

DSV = Dilute solution viscosity (based on concentration of oil-free polymer).
SI = Swelling index (g. benzene held by 1 g. gel rubber).

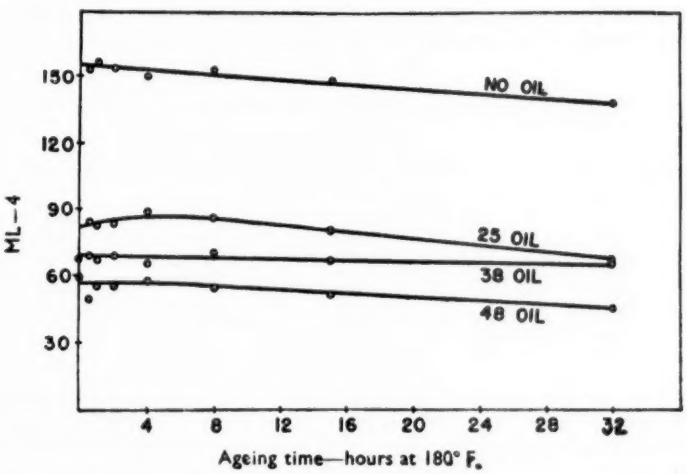

FIG. 3.—Oven aging of oil-polymer master-batches (X-628 base polymer).

Polymers studied were X-628 base polymer containing 0, 25, 38, and 48 parts Circosol-2XH, and standard cold rubber (GR-S-101) as control.

Heating of the oil-free base polymer caused a moderate drop in Mooney viscosity, a marked reduction of DSV, a moderate drop of gel content, and a small increase of swelling index of the gel. The polymer with 25 parts oil exhibited a moderate drop of Mooney viscosity, a moderate reduction of DSV, very little change of gel content, and slight change of swelling index. With 38 parts of oil, the Mooney viscosity was practically unchanged, the DSV values dropped slightly, the gel content increased with heating, and swelling index values dropped from initially very high values. The polymer with 48 parts of oil exhibited a moderate drop in Mooney viscosity, a slight drop in DSV value, a large increase of gel content in the latter portion of the heating period, and a large drop in swelling index values. In comparison, the cold rubber control was practically unchanged during the heating period.

It is interesting to speculate on the effect of the oil on the polymer. Clearly, the addition of oil exerts a solubilizing effect on the gel initially present in the polymer. When the masterbatch is heated, the oil evidently acts as a "protective diluent," and minimizes chain scission reactions, as evidenced by the fact that DSV values tend to remain higher than in the absence of oil. At the same time, the gel content tends to increase as heating is continued, and this tendency is accentuated in the presence of increased oil. The gel content of the polymer with 48 parts of oil, for example, rose to 70 per cent at the end of the heating period, and had a swelling index of only 57. The data strongly suggest that, under the aging conditions studied, dilution of polymer with oil decreases the frequency of chain scission reactions and allows cross-linking reactions to predominate.

AGING OF OIL–MASTERBATCHED POLYMER OF COLD RUBBER TYPE

The effect of oil addition on the oxidation rate of unvulcanized cold rubber (GR-S-100) was measured. Samples were prepared by adding Circosol-2XH to a benzene solution of GR-S-100 to provide samples containing 25, 37.5, and 50 parts of oil per 100 parts polymer. Oxygen absorption was measured on a thin film obtained by evaporation of the solvent. Data are summarized in

TABLE 6

EFFECT OF ADDITION OF CIRCOSOL ON OXIDATION OF GR-S-100

Time (hours)	Per cent oxygen absorbed at 100° C			
	No oil added	25 parts oil	37.5 parts oil	50 parts oil
0	0	0	0	0
48	0.37	0.35	0.29	0.26
120	0.69	0.66	0.58	0.50
168	0.85	0.81	0.71	0.61
216	1.2	0.98	0.87	0.71
288	2.4	1.2	1.1	0.85
336	3.6	1.5	1.2	0.97
385	5.1	1.9	1.4	1.1
456	8.5	2.3	1.7	1.2

Table 6, where the values given for per cent oxygen absorbed were calculated on the total sample of oil plus polymer. They are also plotted in Figure 4.

These data show a marked decrease in oxygen absorption rate with increasing oil content. This is interpreted to mean that the oxidation rate of the oil is at least small relative to that of the polymer. It is not clear whether the oil acts

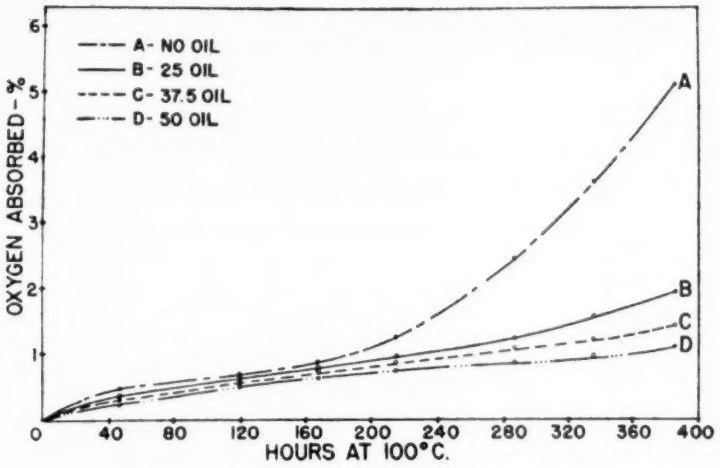

FIG. 4.—Effect of addition of Circosol on oxidation of GR-S-100.

only as an inert diluent or whether it undergoes oxidation at a slow rate more or less independent of the oxidation of the polymer. From a practical standpoint, these data demonstrate that the aging of the unvulcanized polymer is probably improved by the addition of Circosol-2XH.

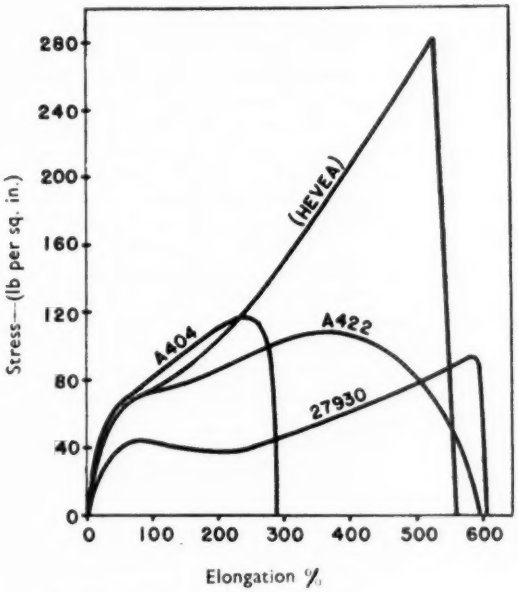

FIG. 5.—Stress-strain curves of raw factory-processed oil polymer tread stock.

STRESS-STRAIN CHARACTERISTICS OF UNCURED COMPOUNDS

Although the improvements in physical properties which could be secured by the use of higher molecular-weight polymers were recognized very early in the synthetic rubber program, progress in this direction was limited by the processing difficulties involved. High molecular-weight polymers have a tendency to be tough and elastic, and are unusually sensitive to any cross-linking or gel formation which occurs during processing. In the development of new oil polymers or oil polymer compounds, processing difficulties associated

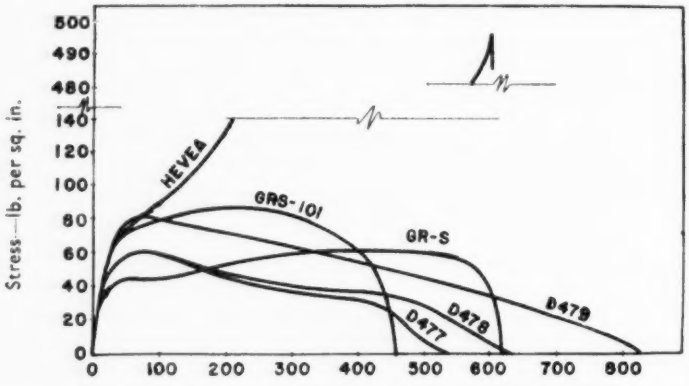

FIG. 6.—Stress-strain curves of raw laboratory-processed tread stocks.

with high molecular weight may be encountered. In some cases, these troubles take the form of a proclivity of the raw compound to crack or tear, due to a predominantly elastic rather than plastic response to the processing deformations. The measurement of the plasticity of the stock is not entirely adequate to anticipate or understand such processing behavior. It has been found that determination of the tensile stress-strain characteristics of the uncured compound may be very informative in regard to certain types of processing deficiencies, especially in regard to tendencies of a tread compound to crack or tear or open the splice on uncured expanded tires.

The technique for measuring the stress-strain characteristics of an uncured tread compound requires the preparation of uniform test-pieces. These can be die-cut from test sheets pressed out between aluminum foil to a thickness of 0.08 inch. A press time of five minutes at 230° F is usually adequate. The sheet is cooled under pressure, and a period of 24 hours is allowed between pressing the sheets and the tensile tests.

The load-elongation curves were recorded with an Instron Tester[9]. This is particularly well adapted for such work because of the low load range available and the smoothness of the jaw motion.

Figure 5 illustrates the diverse character of the stress-strain curves for several experimental factory-processed oil polymer tread stocks and a natural rubber control. Compound A404, which had a high modulus at low elongations and a low ultimate elongation, was distinctly inferior in processing behavior and could not be used in the factory. A422 was a borderline case for processing, whereas 27930 was satisfactory.

Stress-strain curves for three uncured oil polymer tread compounds processed in the laboratory are shown in Figure 6.

Comparison with the regular GR-S and cold rubber controls indicates that these oil polymer stocks should be satisfactory for building tires. There is shown an interesting systematic increase of ultimate elongation with increasing styrene content for the oil polymers.

This new, simple technique has been instructive also for observation of the effect of the various steps in processing on the stress-strain curves and hence on the processibility.

The method has been effective for examining raw polymers before any compounding[10].

In this case, it is necessary to press out the sheets for about two hours at 300° F. In addition, it is desirable to clamp them flat between plates during the twenty-four hour period before testing to minimize shrinkage and distortion.

Figure 7 is a plot of the 100 per cent modulus secured in this way for a series of raw polymers for which parts of modifier in the polymerization recipe and the oil content were systematically varied. A value for the 100 per cent modulus of about 20 lb. per sq. in. for the raw oil polymer masterbatch, determined by this test, appeared to be about the maximum permissible for satisfactory factory processing of the tread stock. This value, of course, will be subject to considerable variation, depending on the details of processing and the type of compounding.

OIL-MASTERBATCHED ALFIN POLYMERS

Synthetic rubbers prepared with alfin catalysts are particularly well adapted to the oil-masterbatching technique[11]. The alfin process[12] produces soluble

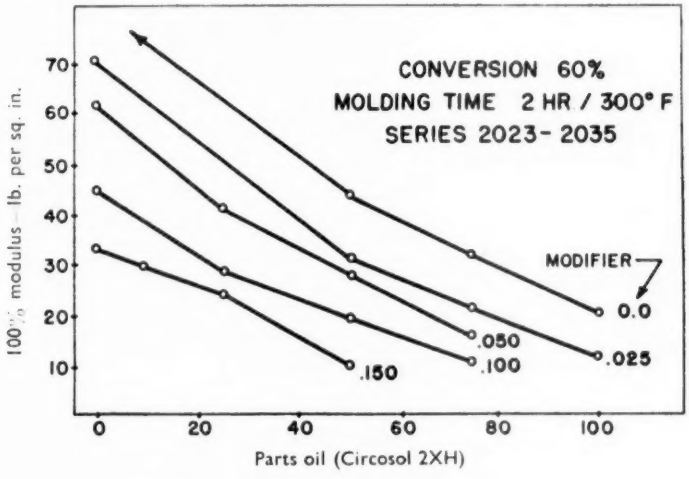

FIG. 7.—100% modulus of uncompounded polmers.

polymers of extremely high molecular weight. The reaction is carried out in a hydrocarbon solvent such as pentane. Upon completion of the polymerization reaction, rubber processing oils are added and thoroughly incorporated before evaporation of the solvent. In this way, 100, or even 200, parts of oil per 100 parts of polymer can be added to give an oil-masterbatch which processes more

easily than the very tough, oil-free base polymer. The oil can also be added to the polymer after it has been isolated, or it can be added with the monomers as a partial or total replacement for the solvent prior to polymerization.

TABLE 7

RAW POLYMER PROPERTIES OF OIL-MASTERBATCHED ALFIN POLYMERS

Alfin polymer B/S	Circosol-2XH PHR	ML/4	DSV of masterbatch
100/0	0	—	8.7 (30% gel)
	100	44	3.3
	150	32	3.1
	200	21	3.0
80/20	0	98*	8.7
	26	73	5.3
	51	56	4.5
	75	41	4.0
	132	22	2.4
	160	17	2.4
	190	—	1.8

* Value questionable because of extreme toughness of polymer.

The high molecular-weight of alfin polymers is strikingly demonstrated by DSV values of the polymers and their oil masterbatches.

As much as 200 parts of oil per 100 parts of polymer are required to reduce the DSV value of an alfin polymer to that of GR-S or cold rubber, as summarized in Table 7.

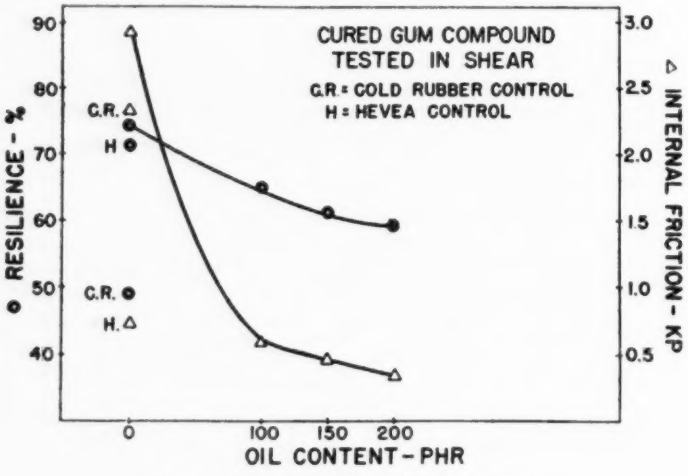

FIG. 8.—Dynamic properties of alfin polybutadiene.

The extremely high molecular weight of alfin polymers is also responsible for the unusually high resilience values exhibited by them and their oil masterbatches. Their dynamic properties are superior to those of cold rubber and approach those of Hevea.

Results for the raw polymer and for the cured gum stock tested in shear and in compression as determined on the Goodyear Vibrotester are given in Table 8 and plotted in Figure 8 for alfin polybutadiene and its oil masterbatches with 100, 150, and 200 parts Circosol-2XH.

TABLE 8

DYNAMIC PROPERTIES OF ALFIN POLYBUTADIENE CONTAINING OIL

Code	Parts oil (Circosol-2XH) per 100 parts rubber	Raw tested in shear polymer			Cured gum compound (40/275) tested in shear			Cured gum compound (40/275) tested in compression		
		Dynamic shear modulus (kg./cm.²)	Internal friction (kilo-poises)	Resilience (%)	Dynamic shear modulus (kg./cm.²)	Internal friction (kilo-poises)	Resilience (%)	Dynamic shear modulus (kg./cm.²)	Internal friction (kilo-poises)	Resilience (%)
23-A	0	30.5	4.4	70.5	23.5	2.92	74.0	97.8	12.1	74.1
23-B	100	6.72	1.71	59.0	3.28	0.59	64.7	15.78	2.86	64.5
23-D	150	4.59	1.075	56.8	2.34	0.47	61.2	10.8	2.17	61.4
29-A	200	2.67	0.72	52.0	1.63	0.35	59.3	7.30	1.63	58.3
Cold rubber	0	5.26	1.78	44.5	7.95	2.35	49.0	38.0	10.62	50.8
Hevea	0	4.29	0.792	63.9	5.27	0.736	71.3	27.2	3.125	75.7

Addition of 100 parts of oil markedly reduces internal friction and only moderately reduces resilience. Additional amounts of oil exert a relatively small effect on these properties.

Table 9 lists the properties of tread stocks of alfin polybutadiene and butadiene/styrene 80 and 70/30 copolymers masterbatches with various amounts of Circosol-2XH and compounded with various amounts of HAF (high abrasion furnace) carbon black. The polybutadiene stocks contained 150

TABLE 9

TREAD STOCK PROPERTIES OF ALFIN POLYMER OIL–MASTERBATCHES

B/S ratio		100/0	100/0	80/20	80/20	70/30	Cold rubber
Parts polymer		100	100	100	100	100	100
Parts Circosol-2XH		150	150	75	100	50	—
Parts HAF Black		125	162.5	87.5	120	75	50
				Stress-strain			
300% modulus							
20′/275°			650	475	550	500	350
40		400	750	600	700	650	875
80			775	670	775	800	1350
Tension strength (lb./sq. in)							
20			1600	2600	2100	2625	1450
40		1600	1800	2550	2160	2650	3059
80			1950	2700	2200	2600	3550
Elongation, 20%			540	820	750	780	880
40		630	550	740	690	710	700
80			540	700	640	650	600
				Goodyear-Healy rebound			
Cold 55			49.2	56.0	46.9	50.1	57.5
95			49.2	56.0	48.3	50.1	58.5
Hot 55			64.2	74.1	67.9	72.4	68.5
95			64.2	75.2	69.6	73.0	70.7
				Goodrich flexometer			
Shore hardness							
55			49	45	45	50	58
95			50	45	45	50	59
Per cent set							
55			5.8	1.6	3.4	1.5	5.3
95			5.0	1.5	2.8	1.2	2.1
Static compression							
55			.377	.357	.380	.325	.225
95			.386	.355	.370	.320	.217
Temperature rise (° F)							
55			60	40	53	40	61
95			59	40	50	40	56

parts of oil and produced tension strengths of less than 2000 lb. per sq. in. An 80/20 butadiene/styrene copolymer containing 75 parts of oil and 87.5 parts carbon black gave a good balance of properties. The tensile strength approached that of the cold rubber control, and the resilience values were superior, measured by rebound values and temperature rise in the Goodrich flexometer. A 70/30 copolymer containing 50 parts of oil and 74 parts carbon black also gave data approximately equal to those of the cold rubber control, but with a definite reduction in temperature rise.

Alfin polymers with these large oil contents tend to stick to the mill rolls during mixing operations. Addition of release agents will probably be necessary for satisfactory large-scale operations.

Effect of Type of Oil

Most of the work reported was done with oil masterbatches containing Circosol-2XH, a naphthenic type of rubber processing oil. Equally satisfactory results have been obtained with a wide variety of other rubber processing oils, containing varying amounts of aliphatic, naphthenic, and aromatic type of components. It is not believed that the chemical composition of the petroleum oil, within the range studied, is of major importance in its effect on the properties of vulcanizates of oil-masterbatched polymers. The superior properties of these masterbatches are inherently due to the high molecular weight of the base polymer, and the function of the oil is largely that of a diluent or internal lubricant. There are some indications, however, that oils of high aromatic content, when used in relatively large amounts (up to 50 parts), demonstrate a greater plasticizing effect than oils of lower aromatic content (and hence poorer solvation characteristics). It is considered important that the oil be free of metallic contamination or other impurities which might act as catalysts for oxidation or other degradation processes, since, under these conditions, the quality due to high molecular weight in the base polymer might be dissipated.

ANALYSIS FOR OIL CONTENT OF OIL MASTERBATCHED POLYMERS

A procedure was worked out for the determination of the oil content by extracting with acetone the thinly sheeted out (0.020 inch thickness or less) masterbatch containing Circosol-2XH. Four successive 30-minute extractions at the reflux temperature completely removed the oil, as well as other materials from the base polymer (antioxidant, fatty or rosin acid). An approximate correction can be made for these non-oil materials, but an exact determination of the oil content is not possible unless a portion of the base polymer is acetone-extracted and a suitable correction made for the acetone soluble portion of the base polymer.

EFFECTS OF EXTRACTION OF OIL FROM THE POLYMER ON THE PHYSICAL PROPERTIES

The oil in oil-polymer compounds serves as a sort of internal molecular lubricant. The strong affinity between the oil and the polymer molecules becomes apparent in observations of the osmotic pressure or swelling pressure of the oil for the polymer. These pressures are of the order of 500 lb. per sq. in. It is interesting to compare some of the physical properties of vulcanized oil polymers with those secured after extraction of the oil.

Figure 9 shows stress-strain curves for a gum stock prepared from an oil polymer containing 25 parts of oil (X-628), before and after extraction with acetone. As might be expected, the effect of extraction is to raise the modulus. It is not obvious, however, that the tensile strength and elongation should be decreased in such a way as was actually found. The experiment shows the importance for the tensile properties of secondary valence forces between the molecules, which are affected by the oil. It may be considered that the primary valence cross-linking bonds were not appreciably changed by the extraction. The oil evidently acts in such a way as to insure a better cooperative action of the cross-linked structure of long-chain molecules when stress is applied. Figure 10 shows the results of the same type of experiment with a tread stock, the oil polymer for which contained 45 parts of oil. Again, tensile strength and ultimate elongation were reduced by the extraction.

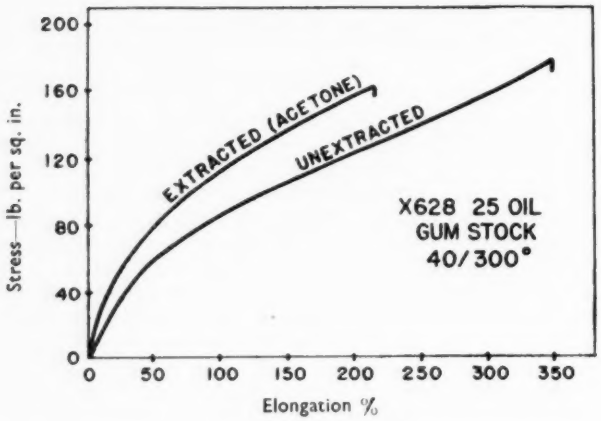

FIG. 9.—Stress-strain curves for an oil-extended gum stock showing effect of oil extraction.

The effect of extraction on hysteresis loops for the gum stock is shown in Figure 11. These loops were secured with the Instron tester. The effectiveness of the oil for reducing the energy loss due to internal friction is readily apparent by visual comparison of the areas of loops. Figure 12 illustrates that the effect is even more pronounced for a tread compound.

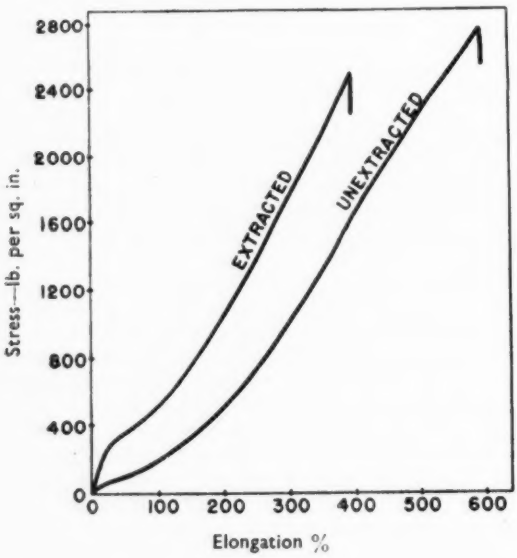

FIG. 10.—Stress-strain curves showing effects of oil extraction on tensile properties of a tread stock.

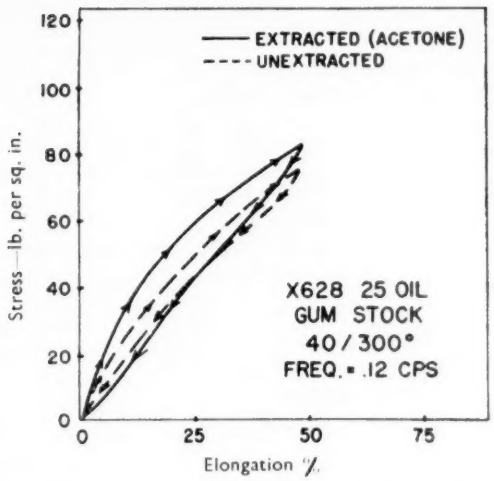

FIG. 11.—Low frequency hysteresis curves for extracted gum stock, showing effect of oil on resilience.

OIL SORPTION STUDIES ON NATURAL AND SYNTHETIC RUBBERS

It was considered of interest to conduct some laboratory studies on oil sorption by solid polymers, although it was recognized that it was not as convenient a process as latex masterbatching. Pale crepe and the high molecular-weight base polymer of X-628 were sheeted out in two passes through a warm mill at a 0.035 inch setting between the rolls. Five-gram samples were weighed and immersed in 125 grams of Circosol-2XH maintained at room temperature.

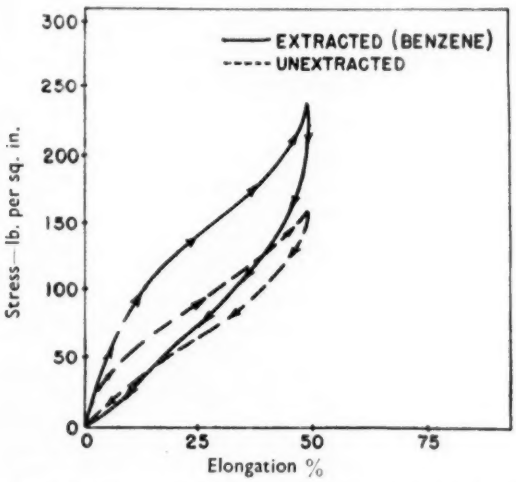

FIG. 12.—Low frequency hysteresis curves showing effect of oil extraction on resilience of a tread stock.

Very substantial oil absorption occurred, as shown by the following set of duplicate values:

Oil absorption (parts oil per 100 parts polymer)	Pale crepe	X-628 base polymer
After 1 day(s)	85, 87	14, 19
After 8 day(s)	292, 316	56, 60
After 40 day(s)	701, 740	138, 131
After 55 day(s)	— —	161, 151
After 63 day(s)	— —	176, 171

Approximately 1 per cent of the polymer was dissolved by the oil. The results are plotted in Figure 13. A constant rate of oil absorption has been at-

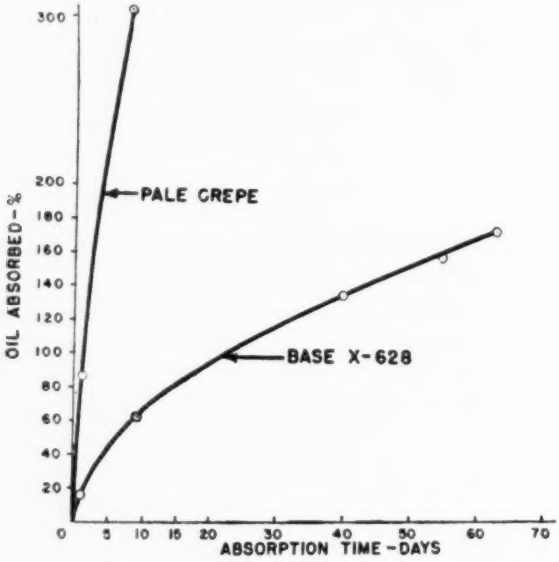

FIG. 13.—Absorption of Circosol-2XH by pale crepe and base X-628 polymer.

tained by the X-628 base polymer, corresponding to about 0.6 part oil per 100 parts polymer per day. Pale crepe, as expected, absorbed oil at a much more rapid rate than the synthetic polymer.

FLEX LIFE OF OIL POLYMER TREAD STOCKS

A new type of flex test was used to secure a laboratory comparison of the durability of oil polymer tread compounds in comparison with GR-S and natural rubber.

In this test, a square test-sheet is held by grips on all four sides. It is then alternately stretched in the two perpendicular directions by means of a rotating cam which alternately separates the pairs of grips. It is a crack growth test, the sheet being punctured in the center by an 0.03 inch diameter needle. The end-point is reached for a crack length of one-half inch. This condition of straining is more severe than the usual uniaxial flex test, and corresponds in an

exaggerated way to the type of cyclic deformation which is experienced in the tread and sidewall of a tire. Figure 14 shows comparative results of this type of flex life test for two oil polymer tread compounds and GR-S, cold rubber, and natural rubber controls. None of the synthetic-rubber compounds approached natural rubber in this test. One of the oil polymer compounds was inferior to the cold-rubber control, but the other three were definitely superior, with best results obtained from the two masterbatches with 25 parts of oil. It may be inferred that oil polymers, properly compounded, are capable of demonstrating substantial improvement in durability over cold rubber.

TABLE 10

DYNAMIC PROPERTIES OF OIL POLYMER TREAD STOCKS

			Dynamic modulus (kg./sq. cm.)		Internal friction (kilopoise)		Resilience (per cent)	
			Uncured	Cured*	Uncured	Cured	Uncured	Cured
Hevea			13.3	21.2	5.92	9.80	34.0	32.3
Cold rubber			20.7	27.0	13.5	15.6	20.8	24.6
GR-S			14.1	24.2	11.0	14.2	15.3	24.3
	B/S	Parts oil						
D-367	80/20	45	12.0	16.8	7.21	9.90	23.3	23.9
D-472	80/20	45	11.4	14.8	6.56	8.37	24.9	25.7
D-471	80/20	25	14.3	18.1	7.93	9.60	26.0	27.5
D-368	75/25	45	11.1	16.3	6.88	10.3	22.2	21.6
D-477	75/25	25	13.4	19.4	6.91	9.73	28.7	29.7
D-478	68/32	25	16.0	20.6	9.33	12.1	24.4	24.0
D-479	60/40	25	14.5	20.4	9.03	14.3	22.2	18.5

* 40/275°.

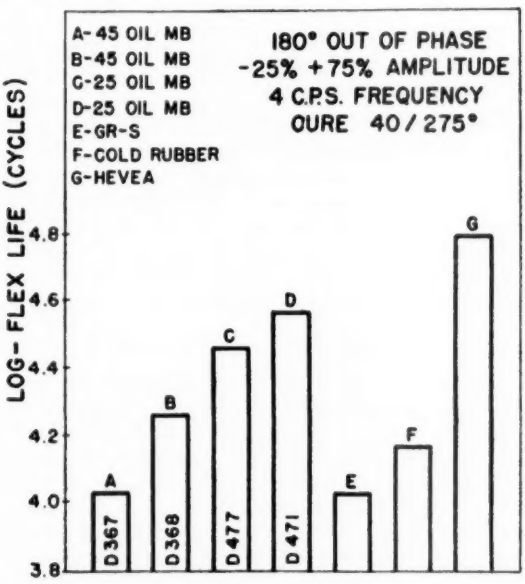

FIG. 14.—Comparative flex life in biaxial strain fatigue test.

DYNAMIC PROPERTIES OF OIL POLYMER TREAD STOCKS

Measurements of the response of polymers to vibratory forces are indicative of their rubberlike quality as well as being of significance for estimating relative heat generation and temperature rise in service. Table 10 gives the results of measurements of dynamic properties for a series of oil polymer tread stocks, before vulcanization and at best cure. Shear vibrations were used, the test-pieces being disks 0.75 inch diameter and 0.125 inch thick. Otherwise, the method for obtaining the data was similar to that already described[13].

A very interesting generalization appears in these data. The internal friction of the uncured oil polymer tread stocks is definitely lower than that for the cold rubber and GR-S controls, so that the resilience of the uncured oil polymer compounds is distinctly superior to that of the synthetic controls, although not as good as the Hevea control. On vulcanization, a large improvement in resilience occurs with the GR-S and cold rubber compounds, whereas, for the oil polymers, improvement in resilience due to vulcanization is small. As a

TABLE 11

STATIC AND KINETIC FRICTION ON ICE TEMPERATURE, −20° C

			Coefficient of friction		
			Static	Kinetic (0.006 in./sec.)	Kinetic (29 in./sec.)
Hevea			0.30	0.23	0.23
Cold rubber			0.33	0.23	0.22
GR-S			0.32	0.21	0.23
	B/S	Parts oil			
D-367	80/20	45	0.28	0.23	0.21
D-472	80/20	45	0.25	0.22	0.22
D-471	80/20	25	0.37	0.26	0.22
D-368	75/25	45	0.32	0.23	0.21
D-477	75/25	25	0.30	0.21	0.19
D-478	68/32	25	0.27	0.18	0.15
D-476	60/40	25	0.18	0.14	0.12

consequence, the original uniform superiority in resilience of the unvulcanized oil polymer compounds is scarcely maintained after vulcanization. Although several of them are distinctly superior in resilience to the controls after vulcanization, most of them become comparable in resilience to the controls. In other words, vulcanization did a great deal more for the resilience of the GR-S and cold rubber controls than it did for that of the oil polymers. This raises a question as to whether or not a more effective system of vulcanization for improving the dynamic properties of oil polymers might be found.

FRICTIONAL PROPERTIES OF OIL POLYMER TREAD STOCKS

The relationship between oil and low friction and the importance of friction for tire traction led to a careful study of the frictional properties of oil polymers. A turn-table type of laboratory apparatus was used for this work[14], which gave more reproducible and precise results than can usually be secured in friction tests, which are notorious for variability. This inherent variability is usually due to difficulty in controlling the character of the surfaces involved and the many other experimental factors which may affect the results.

To determine static friction on ice, the test-pieces were loaded, about 30 lb. per sq. inch, on the ice for 10 minutes (after having been at the test temperature for 10 minutes). The turn-table was then moved with an exceedingly low

TABLE 12

KINETIC FRICTION ON STEEL TEMPERATURE, 25° C

			Coefficient of friction (0.006 in./sec.)
Hevea			0.53
Cold rubber			0.56
GR-S			0.51
	B/S	Parts oil	
D-367	80/20	45	0.62
D-472	80/20	45	0.69
D-471	80/20	25	0.73
D-368	75/25	45	0.66
D-477	75/25	25	0.65
D-478	68/32	25	0.68
D-479	60/40	25	0.73

velocity and the peak force on the test pieces recorded, before sliding occurred, by means of the reaction on a stiff cantilever spring, to which resistance strain gauges were attached. The output of the strain gauges was recorded with a high-speed pen and ink recorder. When sliding occurred, the lower frictional force was indicated on the same record. The results with this method are given in Table 11.

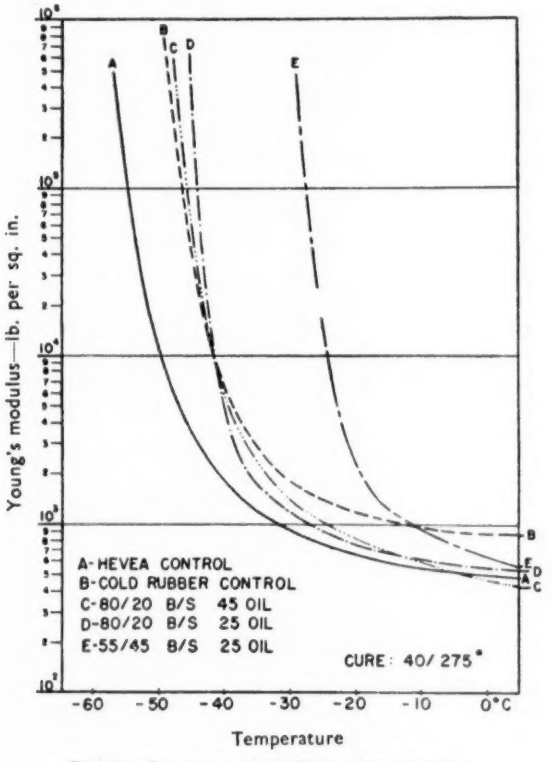

FIG. 15.—Low-temperature stiffening of tread stocks.

Except for the high-styrene polymers, it can be concluded that the oil polymers, as a class, had frictional properties on ice which were very similar to the control compounds. The deleterious effect of high styrene content for friction on ice is noteworthy.

The coefficient of friction for these compounds was measured also against a steel surface carefully prepared by lapping with 350 mesh emery powder. The results are given in Table 12.

Here the friction values are definitely higher for the oil-polymer tread stocks than for the controls. Curiously, the last three compounds show increasing friction with increasing styrene content, just the reverse of what was found on ice.

LOW TEMPERATURE STIFFENING

The curves in Figure 15 show the low-temperature stiffening of several oil-polymer tread stocks compared to natural rubber and cold rubber compounds. A torsional flexibility method[15] was used to secure these results.

The low-temperature stiffening characteristics of the oil-polymer tread stocks were similar to those of the cold-rubber tread stock. The variation in oil content from 25 to 45 parts had remarkably little effect on the low temperature stiffening. As the pour point of the oil used was rather high, about 15° F (−9.4° C), it cannot be expected that the oil should be very efficacious as a low-temperature plasticizer for actually improving low-temperature flexibility. There is some possibility of small variations of styrene content which might affect the relative positions of the curves slightly. The effect of a large variation in styrene content is evident in the high stiffening temperatures found for D479.

Table 13 gives the temperature at which the stiffness increases from that at

TABLE 13

LOW TEMPERATURE STIFFENING OF OIL–POLYMER TREAD STOCKS

			T_2	T_5	T_{10}	T_{100}
Hevea			−30° C	−42° C	−46° C	−56.5° C
GR-S			−25	−38.5	−43	−52
Cold rubber			−27.5	−36.5	−40.5	−49
	B/S	Parts oil				
D-471	80/20	25	−27	−37.5	−39.5	−45
D-477	75/25	25	−20	−33	−36	−43.5
D-478	68/32	25	−16	−26	−30	−36.5
D-479	60/40	25	−10	−20	−22	−29
D-472	80/20	45	−26	−39	−41.5	−48
D-367	80/20	45	−21.5	−35	−38	−47.5
D-368	75/25	45	−22	−31	−34	−41

room temperature by factors of 2, 5, 10, and 100 for a series of oil polymer tread stocks.

LABORATORY TREAD-STOCK DATA ON COLD-RUBBER MASTERBATCHES

Oil-rubber masterbatches have opened up a vast field of exploration for rubber compounders. From this work has come the realization that, in most cases, the masterbatch should be treated as if all of it were rubber hydrocarbon. In all work to be described, this approach has been taken. Table 14 sum-

marizes pertinent data on pilot-plant and production oil-masterbatched polymers used in this work. Table 15 lists laboratory tread-stock data for a series of commercially available oil-polymer masterbatches. They were compounded so as to contain 50 parts HAF (high abrasion furnace) black per 100 parts by weight of masterbatch. Adjustments in proportions of other compounding ingredients were made as necessary.

TABLE 14

DESCRIPTION OF OIL–RUBBER MASTERBATCHES

Type[a]	B/S charge ratio	Combined[b] ratio	Emulsifier	% Conversion	Base[d] polymer Mooney	Oil[e] per p10 polymer	Final ML	Compound code
XP-238	75/25	80/20	Rosin soap	60	145 ML	25	64	D-471
XP-239	75/25	80/20	Rosin soap	60	145 ML	45	58	D-472
XP-225	75/25	80/20	Rosin soap	60	82 MS	45	62	D-367
XP-235	68/32	75/25	Rosin soap	60	84 MS	45	61	D-368
XP-254	68/32	75/25	Mixed soap[c]	60	145 ML	25	66	D-477
XP-246	60/40	68/32	Mixed soap[c]	60	145 ML	25	54	D-478
XP-247	60/50	50/40	Mixed soap[c]	60	145 ML	25	56	D-479
X-628	75/25	80/20	Mixed soap	60	70±5 MS	25	58	—
X-646[f]	75/25	80/20	Fatty acid soap	68	80 ML	25	49	—
X-654	75/25	80/20	Mixed soap	60	70±5 MS	25	64	—
X-660	75/25	80/20	Rosin soap	60	65±5 MS	25	73	—
X-661	75/25	80/20	Rosin soap	60	82±5 MS	50	63	—
X-676	75/25	80/20	Mixed soap	60	70±5 MS	37.5	47	—

[a] XP-polymers produced by Government Evaluation Laboratories, University of Akron, Akron, Ohio. X-polymers produced in Government-owned and industry-operated synthetic rubber plants.
[b] The 80/20 ratios are estimated; the others were obtained by analysis.
[c] A mixture of equal amounts of fatty acid and rosin acid soap.
[d] ML refers to Mooney viscosity obtained with large rotor, and MS to value from small rotor.
[e] Oil employed was Circosol 2XH (Sun Oil Co.) except for X-654, which contained SPX-97 Processing Oil (Shell Oil Co.).
[f] All polymers listed are masterbatches with cold rubber, except X-646, which is a hot rubber masterbatch.

Polymers X-628, X-654, and X-660 are masterbatches containing 25 parts oil per 100 parts polymer, and are compared against a standard cold rubber control, X-624. The data demonstrate that these polymers possess equivalent stress-strain properties, markedly superior abrasion resistance, and definitely superior dynamic characteristics, as indicated by higher Goodyear-Healy rebound values (both hot and cold), and by lower temperature rise on the Goodrich flexometer. Even a masterbatch containing 50 parts of oil per 100 parts of polymer, X-661, gave stress-strain values almost equivalent to the control, and was superior in rebound, temperature rise, and abrasion values.

Additional data are listed in Table 16 for cold rubber (X-624), and masterbatches containing 25 and 37.5 parts oil per 100 parts of polymer (X-628 and X-676, respectively). All of these polymers were produced at the Government synthetic rubber plant at Houston, Texas, operated by Goodyear. The tread stock data are similar to those just described, except that the hysteresis and abrasion resistance characteristics of X-676 are somewhat poorer than expected. The values may have been affected by the relatively low Mooney viscosity (47 ML-4) of this particular sample.

Table 17 lists some interesting tread-stock data on a series of polymers in which the butadiene-styrene charging ratio was varied as follows: X-628 (75/25), XP-254 (68/32), XP-246 (60/40), and XP-247 (50/50). All were

TABLE 15

TREAD-STOCK DATA ON OIL-COLD RUBBER MASTERBATCHES

Polymer		X-624	X-628	X-654	X-660	X-661
ML-4		52	58	64	73	63
300% modulus	20/275°	350	500	500	500	600
	30	650	900	950	800	875
	40	900	1125	1200	1075	1200
	60	1150	1600	1650	1475	1350
	80	1200	1725	1675	1575	1450
Tensile strength (lb. per sq. in.)	20/275°	1525	2800	2025	2100	2100
	30	2575	2850	2900	2950	2600
	40	3000	3000	3200	3250	2900
	60	3200	3350	3300	3350	2900
	80	3000	3300	3350	3400	2950
Elongation (%)	20/275°	900	730	740	710	690
	30	750	640	630	670	610
	40	700	550	610	600	560
	60	630	510	510	530	490
	80	580	470	500	500	490
Hot tensile strength	40	1245	1380	1490	1305	1180
	80	1305	1340	1345	1520	1205
Hot elongation (%)	40	465	425	475	425	390
	80	415	375	375	410	385
Rebound (%)	55	59	62.5	60.5	61.5	60.5
	95	60.5	63.6	61.5	62.0	61.0
Deflection	55	.224	.239	.233	.238	.253
	95	.227	.238	.233	.236	.252
Hot rebound (%)	55	71.8	76.5	74.1	74.1	74.1
	95	73.0	77.6	75.2	75.8	74.6
Deflection	55	.268	.278	.274	.274	.289
	95	.265	2.75	.270	.278	.286
		Goodrich flexometer				
Shore hardness	55	55	55	51	55	52
	95	59	59	59	57	55
Set (%)	55	4.5	3.1	2.9	3.1	3.1
	95	1.8	1.5	1.5	1.6	1.7
Static compression	55	.259	.246	.244	.241	.294
	95	.230	.229	.220	.233	.220
Temperature rise	55	59	49	53	51	54
	95	63	45	47	45	49
Ring abrasion (cc. loss)	55	6.45	3.40	3.20	3.70	3.40
	95	6.45	3.27	3.21	3.49	3.40
		Road wear rating				
		100	123	—	122	—
		100	121	—	—	110
		100	120	117	—	—

TABLE 16

TREAD-STOCK DATA ON OIL-COLD RUBBER MASTERBATCHES
(25 *v.* 37.5 parts oil)

		X-624	X-628	X-676
ML-4		50	57	47
300 per cent modulus	30/275°	1150	1050	1175
	40	1300	1300	1450
	60	1600	1675	1650
Tensile strength (lb. per sq. in.)	30	2750	2850	2700
	40	2950	3000	3150
	60	3100	3000	3300
Elongation (per cent)	30	620	630	590
	40	610	570	570
	60	530	470	530
Hot tensile strength	40	1370	1420	1460
	80	1410	1215	1540
Hot elongation (per cent)	40	450	465	445
	80	400	355	415
Rebound (per cent)	55	58.5	62.5	61.0
	95	60.0	63.6	62.0
Deflection	55	.218	.239	.207
	95	.215	.236	.207
Hot rebound (per cent)	55	68.5	73.0	66.2
	95	69.6	75.2	67.9
Hot deflection	55	.257	.229	.247
	95	.253	.275	.243
Ring abrasion (cc. loss)	55	4.45	3.20	4.30
	95	4.50	3.10	4.10
	Goodrich flexometer			
Shore hardness	55	65	60	64
	95	65	60	64
Set (per cent)	55	1.2	1.2	0.8
	95	1.1	1.2	1.5
Static compression	55	.200	.190	.176
	95	.200	.230	.185
Temperature rise (° F)	55	40	33	45
	95	40	36	49

masterbatches with 25 parts oil per 100 parts polymer, and the final viscosity values were in the range 54 to 66 ML-4. The data reflect remarkably little change in properties as the monomer ratio was changed over a rather wide range. The stress-strain data are similar, except that the three polymers of highest styrene content exhibited significantly higher hot tensile strengths than the control polymer X-628. The hot rebound values were practically identical, but in cold rebound the polymer of highest styrene content was significantly poorer. Practically identical results were obtained for abrasion resistance and

TABLE 17

TREAD-STOCK DATA ON OIL MASTERBATCHES WITH POLYMERS OF VARYING STYRENE CONTENT

		X-628	XP-254	XP-246	XP-247
Charge ratio		75/25	68/32	60/40	50/50
Combined ratio		80/20	75/25	68/32	60/40
ML-4		58	66	54	56
300 per cent modulus	30/275°	900	875	775	660
	40	1125	1000	1050	975
	60	1500	1425	1475	1400
Tensile strength (lb. per sq. in.)	30	2400	2500	2500	2500
	40	2850	2850	2750	2700
	60	3050	3000	3075	3025
Elongation (per cent)	30	600	690	730	800
	40	575	610	630	640
	60	510	550	540	560
Hot tensile strength	40	1175	1575	1385	1510
	80	1255	1500	1560	1420
Hot elongation (per cent)	40	350	530	490	575
	80	350	345	425	410
16 hrs. air bomb	40	1550	1550	1600	1600
300 per cent modulus	80	1900	1800	1850	1900
Tensile strength	40	2300	2375	2400	2350
	80	2250	2150	2450	2400
Elongation (per cent)	40	410	440	470	450
	80	340	340	390	370
Rebound (per cent)	55	61	60.5	59.5	55.6
	95	62.5	62.0	60.0	55.0
Deflection	55	0.239	0.236	.237	0.234
	95	0.237	0.232	0.231	0.228
Hot rebound (per cent)	55	73.0	72.4	72.4	71.8
	95	74.6	74.1	74.6	74.1
Hot deflection	55	0.281	0.279	0.282	0.291
	95	0.273	0.272	0.276	0.292
Ring abrasion (cc. loss)	55	3.20	3.30	3.60	3.85
	95	2.90	3.10	3.35	3.50
		Goodrich flexometer			
Shore hardness	55	56	56	56	55
	95	57	58	58	57
Set (per cent)	55	4.0	4.2	3.3	4.3
	95	1.8	1.8	1.7	1.6
Static compression	55	0.195	0.195	0.205	0.204
	95	0.216	0.207	0.203	0.210
Temperature rise	55	32	32	34	34
	95	34	34	34	34

TABLE 18

TREAD-STOCK DATA ON OIL-HOT RUBBER MASTERBATCHES

Polymer		GR-S-20	P4586	X-646
ML-4		47	48	49
300 per cent modulus	30/275°	525	450	700
	40	560	650	950
	60	775	800	1150
Tensile strength (lb. per sq. in.)	30	1850	1850	1900
	40	2100	2100	2300
	60	2050	2350	2150
Elongation (per cent)	30	730	750	600
	40	680	650	570
	60	610	620	470
Rebound (per cent)	55	56.5	58.0	61.5
	95	58.0	59.0	63.1
Deflection	55	0.239	0.250	0.248
	95	0.235	0.250	0.244
Hot rebound (per cent)	55	66.2	67.3	70.7
	95	67.3	68.5	71.8
Deflection	55	0.281	0.302	0.283
	95	0.279	0.297	0.280
Ring abrasion (cc. loss)	55	8.90	5.78	7.40
	95	8.75	6.18	7.20
Goodrich flexometer				
Shore hardness	55	56	51	54
	95	57	52	55
Set (per cent)	55	6.8	6.9	3.6
	95	3.0	2.7	1.7
Static compression	55	0.309	0.328	0.284
	95	0.292	0.298	0.258
Temperature rise (° F)	55	64	60	51
	95	59	53	47
Road test data				
Fast wear route		100	119.5	131.5
		100	125.5*	—
Regular wear route		100	*V* 109.5	113

* An independent test with another Goodyear pilot plant preparation of hot rubber-oil masterbatch.

temperature rise on the Goodrich flexometer. The data suggest that, in the range studied, molecular weight is a more important determinant of physical properties than butadiene-styrene ratio.

LABORATORY TREAD-STOCK DATA ON HOT-RUBBER MASTERBATCHES

The concept of masterbatching with oil was also extended to hot rubber, or regular GR-S. Table 18 lists tread-stock data on a Goodyear pilot plant

TABLE 19

TREAD-STOCK DATA ON OIL-RUBBER MASTERBATCHES WITH VARIATION IN CARBON BLACK

		Cold-rubber tread HAF black			Hot-rubber tread EPC/HMF black		
		X-624	X-628	P4586	X-611	X-628	P4586
ML-4		56	64	32	56	64	32
300% molulus	30/275°	640	800	575	550	350	550
	40	875	1200	850	750	600	650
	60	1025	1550	1100	875	1000	875
Tensile strength (lb. per sq. in.)	30	2500	2000	1500	1850	1125	1800
	40	2850	2150	2000	2600	2400	2200
	60	3100	2925	2350	2550	2850	2250
Elongation (%)	30	770	570	600	690	660	680
	40	690	540	550	680	700	560
	60	630	480	520	620	610	580
Rebound (%)	55	59	60.5	55.5	58.5	61.0	58.0
	95	60.0	62.0	56.5	59.5	62.0	59.0
Deflection	55	0.224	0.232	0.234	0.225	0.239	0.252
	95	0.222	0.229	0.231	0.222	0.234	0.249
Hot rebound (%)	55	69.6	70.1	64.2	70.7	69.0	69.0
	95	71.8	73.1	66.7	72.4	73.0	64.6
Deflection	55	0.261	0.270	0.289	0.264	0.279	0.305
	95	0.258	0.262	0.278	0.257	0.269	0.295
Ring abrasion (cc. loss)	55	7.30	4.00	4.60	10.00	6.78	6.70
	95	6.85	3.75	4.00	9.90	6.32	6.40
		Goodrich flexometer					
Shore hardness	55	55	54	50	54	53	50
	95	59	59	54	56	55	50
Set (per cent)	55	4.8	7.1	15.5	4.0	7.3	6.6
	95	2.4	1.9	6.0	1.6	2.1	2.9
Static compression	55	0.242	0.225	0.305	0.255	0.295	0.333
	95	0.206	0.227	0.275	0.240	0.256	0.316
Temperature rise (° F)	55	58	60	80	54	60	60
	95	55	50	65	50	50	55
		Road wear					
Fast wear route		100	123.4	100.5	100	171	102

masterbatch, P4586, and a similar masterbatch prepared at the Houston plant, X-646, in comparison with GR-S-20 as the GR-S control. The base polymer for the masterbatches was of higher molecular weight than GR-S, but after masterbatching with 25 parts of oil, they exhibited Mooney viscosities equivalent to the control. From examination of the data it can be concluded that the masterbatches possess equivalent stress-strain values, but are somewhat superior in rebound, temperature rise on the Goodrich flexometer, and abrasion resistance.

In Table 19 an interesting comparison is drawn between cold rubber (X-624

TABLE 20

SUMMARY OF ROAD TEST DATA

Polymer	Cold rubber	Cold rubber 25 oil MB	Hot rubber 25 oil MB	GR-S
Tread wear, relative ratings	100	123, 122	—	—
	100	121	—	—
	100	120, 117	—	—
	100	124	101	—
	100	117	102	—
	—	—	120, 132	100
	—	—	126	100
	—	—	110, 113	100
Average rating	100	121	101.5	—
	—	—	120	100

or X-611), a cold rubber masterbatch (X-628), and a hot rubber masterbatch (P4586). In the first group, all three were compounded with 50 parts HAF (high-abrasion furnace) black, as is customary for a cold-rubber tread. In the second group, the loading was 50 parts of black consisting of an equal mixture of EPC (easy-processing channel) and HMF (high-modulus furnace) which is often used for treads containing hot rubber. In each case, the polymers can be arranged in the same order, with the best overall properties exhibited by X-628, followed in turn by X-634 and P4586. As expected, the chief effect of changing from EPC/HMF black to HAF black is increased abrasion resistance.

TREAD WEAR DATA FROM ROAD TESTS

The ultimate criterion of the worth of any new polymer is its performance under actual service conditions. Enough data have been accumulated to justify some conclusions concerning the tread wear of passenger tires containing tread stocks of oil-masterbatched polymers, tested against cold rubber and GR-S as controls. Some of the tests available to date are listed in Tables 15, 18, and 19, along with the corresponding laboratory data, and are collected for

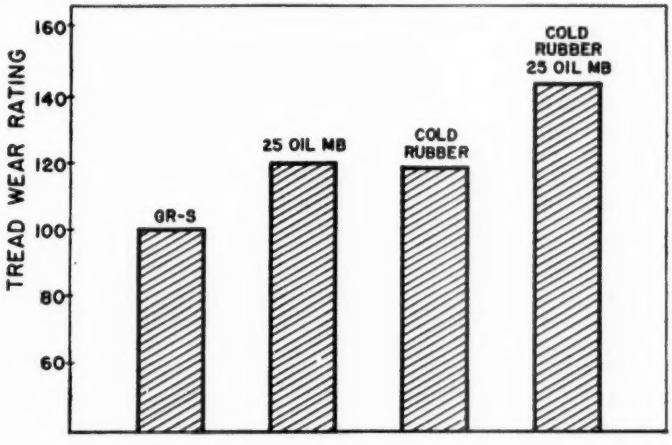

FIG. 16.—Relative tread wear ratings.

easy reference in Table 20. Some of these tests were made privately by Goodyear, others were made on the Government test fleet operated by the Synthetic Rubber Division, Reconstruction Finance Corporation. The data are plotted as barographs in Figure 16.

These data offer convincing proof that tread wear quality is substantially improved by the oil-masterbatching of high molecular-weight synthetic rubbers. The average tread wear rating of GR-S is improved 20 per cent and that of cold rubber is improved 21 per cent by oil-masterbatching of GR-S and cold rubber, respectively. It is probably more than a coincidence that equal improvement was obtained in each case. One test was made with an oil-masterbatch containing 50 parts of oil (X-661). Even with this high dilution, the treadwear rating was 100 against 100 for the cold rubber control (Table 15).

One interesting observation was made in connection with the tire testing program that seems worthy of mention. Tires containing treads compounded with oil-masterbatched polymers exhibited less build-up in static charge than tires containing cold-rubber treads.

To summarize, the treadwear data presented indicate oil-masterbatched hot rubber to be 20 per cent better than GR-S and equivalent to cold rubber, and oil-masterbatched cold rubber to be 21 per cent better than standard cold rubber.

CONCLUSIONS

It seems that the possibilities of this development, both as a lead to improved rubbers and as a spur to the explanation of rubber behavior, are exceptionally stimulating. Far from being a completed work, this is more likely to be the first and exciting chapter of a series yet to be unfolded. It is a distinct possibility that useful improvements to natural rubber, as well as to synthetic, may result from further investigation of the field.

It is perhaps unnecessary to caution that the quantitative relationships developed are not sacrosanct and may be altered by more extensive data. The importance of the results, however, is not entirely dependent on their numerical values.

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COPOLYMERIZATION THEORY OF THE VULCANIZATION OF RUBBER. VI. HYDROGEN SULFIDE EFFECTS AND SOME SELF-LIMITING FEATURES *

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The recent proposal that vulcanization[1] with TMTD[2] as well as with sulfur constitutes a type of copolymerization[3] of rubber-molecule double bonds[4] with sulfur atoms was based in part on the action of hydrogen sulfide. Consequently, a main feature of studies reported here has been to utilize this reagent for relating the various types of vulcanization involving sulfur and certain sulfur compounds.

THE HYDROGEN SULFIDE–TMTD REACTION

The behavior of TMTD in vulcanizing rubber can be considered on the basis of two types of reaction depending on the concentration[3] of H_2S which may be allowed to build up. In the presence of ZnO the concentration will be low, but presumably still high enough to permit the formation of the trisulfide by reactions I and II. The trisulfide, TMTT, possesses the formal requirements of a source of S_2 radicals (reactions III and IV), and, no doubt because of instability, has not been isolated. The H_2S required for reactions I and IV could obviously arise from TMTD and methylenic hydrogen atoms of the

$$\text{TMTD} + H_2S \longrightarrow (S) + 2(CH_3)_2NC(S)SH \rightleftharpoons 2CS_2 + 2(CH_3)_2NH \quad \text{(I)}$$

$$\text{TMTD} + (S) \longrightarrow \text{TMTT} \quad \text{(II)}$$

$$\text{TMTT} \rightleftharpoons \text{TMTM} + \cdot SS\cdot \quad \text{(III)}$$

$$\text{TMTT} + H_2S \longrightarrow \cdot SS\cdot + 2(CH_3)_2NH + 2CS_2 \quad \text{(IV)}$$

$$2\,\text{TMTD} \rightleftharpoons \text{TMTM} + \text{TMTT} \quad \text{(V)}$$

rubber molecules, perhaps leading incidentally to a minor amount of cross-linking. However, since only a small amount of H_2S is required at any time, the initial quantity could come from TMTD itself[5]. Formally, the reversible disproportionation V would be satisfactory as the initial step in TMTD vulcanization except for the fact that it takes no account of H_2S initiation. The shift of V and similar reactions of TMTM with polysulfides higher than TMTT to the left does explain the observation that the compounding of high concentrations of TMTM actually represses TMTD vulcanization. Lower concentrations of TMTM, formed during ordinary TMTD vulcanization appear desirable, since the presence of polysulfides higher than TMTT are thus avoided. These higher polysulfides would be expected to use their sulfur inefficiently as vul-

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canizing agents, since they would lead to the introduction of too many sulfur atoms per cross-link as a result of releasing higher polysulfur radicals. The higher polysulfides and their radicals should also lead to excessive local concentrations of H_2S and thus to too early termination of the copolymerization reaction. Fortunately, TMTD and TMTM are relatively unreactive toward ZnO. Consequently this oxide can exert a buffering action on the acids of vulcanization, in this case, H_2S and the dithiocarbamic acid formed by the action of H_2S on TMTD and TMTM.

In the absence of ZnO or other buffer[3], the H_2S concentration tends to be high and another type of TMTD behavior can be visualized. The dithiocarbamic acid[6] of Equation I decomposes to form dimethylamine, which can act on TMTD by way of reactions VI, VII, and VIII. These by summation give the over-all von Braun reaction[5] IX:

$$3\text{TMTD} + 6\text{HN}(\text{CH}_3)_2 \longrightarrow 3(\text{CH}_3)_2\text{N—C(S)SN}(\text{CH}_3)_2 + 3\text{DMADC}$$

$$\overbrace{6\text{HN}(\text{CH}_3)_2 + 3\text{CS}_2} \quad \text{(VI)}$$

$$3(\text{CH}_3)_2\text{NC(S)SN}(\text{CH}_3)_2 \longrightarrow \text{TMTD} + \text{TMTU} + (\text{CH}_3)_2\text{N—S—N}(\text{CH}_3)_2 \quad \text{(VII)}$$

$$(\text{CH}_3)_2\text{NSN}(\text{CH}_3)_2 + 2\text{CS}_2 \longrightarrow \text{TMTD} + (\text{S}) \quad \text{(VIII)}$$

$$\text{TMTD} \longrightarrow \text{CS}_2 + (\text{S}) + \text{TMTU} \quad \text{(IX)}$$

This formulation in itself cannot account for TMTD vulcanization, because it gives no explanation for the activating effect of ZnO. Also the failure of TMTU, CS_2, and secondary amines (*e.g.*, one PHR of dibutylamine had no effect on the vulcanization of a stock containing 4 PHR of TMTD and 5 PHR of ZnO) to activate TMTD shows that some other mechanism must be operable. Further, the inactivity as vulcanizing agents, in the presence of ZnO, of dimethylamino sulfide of reaction VII and the sulfenamide of reaction VI supports this view. However, equations VI, VII, and VIII do account for the fact, as now reported, that TMTD, though stable at 140° at 0.001 mm., does decompose into TMTU, CS_2, and sulfur if the volatile products[5], CS_2 and $(CH_3)_2NH$, are allowed to accumulate. Bloomfield[7] recently reported a 30 per cent yield of CS_2 to be formed from TMTD at 140° during one hour, but he operated at a pressure so high (atmospheric) that volatile products would not be effectively removed. The TMTM, not reported by him to be formed under these conditions, might be an expected product, but in the light of our work it evidently decomposes into TMTU and CS_2. At an intermediate pressure of 0.35 mm. at 140°, we detected traces of TMTM. During the course of vulcanization most of the TMTM (a thianhydride) disappears as a result of the action of H_2S and ZnO with the formation of ZNDMDC and water. In this connection a semicured TMTD stock was found to contain more TMTM than one fully cured.

The sulfur of equation IX is available for use in reaction II and, to the extent that reaction IX occurs in spite of the presence of ZnO, this represents a source of TMTT alternative to the direct action of H_2S on TMTD.

The van Braun reaction IX formally can also be arrived at from reactions X and XI by summation. However, the stability of TMTD at 140° and 0.001 mm. pressure definitely rules out reaction X as a prime mover in vulcanization.

$$\text{TMTD} \longrightarrow (\text{S}) + \text{TMTM} \quad \text{(X)}$$

$$\text{TMTM} \xrightarrow{(\text{CH}_3)_2\text{NH}} \text{TMTU} + \text{CS}_2 \quad \text{(XI)}$$

$$\text{TMTD} \longrightarrow (\text{S}) + \text{TMTU} + \text{CS}_2 \quad \text{(IX)}$$

This indicated that the initiator is a volatile compound such as H_2S.

The action of a slight excess of radioactive hydrogen sulfide (H_2S^*) on TMTD (0.05 mole) in benzene solution at 30° during five hours led to nearly inactive CS_2 (isolated and counted as DMADC after reaction with dimethylamine) and DMADC. Radiosulfur containing most of the activity of the H_2S^* started with was also isolated. In this work the H_2S^* was not isolated but was used in slight excess directly after preparation from dodecanethiol and radio sulfur, S_8^*, in the presence of a trace of zinc palmitate. Experience with the reaction showed that the disulfide also produced was inactive thus confirming the work of Tarver and Schmidt[8] in the cysteine-cystine-S* system. The data for our experiment are in Table I.

TABLE I

Substance	Radioactivity (c/m)
Sulfur, S_8^*, started with	79.3
TMTD (0.050 mole) started with	0.0
DMADC (0.042 mole) produced, m.p. 135 (dec.)	0.14
DMADC from CS_2 produced (0.050 mole)	0.83
Radiosulfur (0.050 atom) produced, m.p. 120°	65.0

In this experiment some interchange of the sulfur isotopes probably occurred during isolation of the DMADC and sulfur. These data and the finding by Gregg and Tyler[9] that the electrolytic reduction of a tetralkylthiuram disulfide to the corresponding dialkyl dithiocarbamate ion is rapidly reversible suggests the following simple mechanism (compare reaction I) for the course of this reaction. The controlling step in the process with excess hydrogen sulfide is

$$(CH_3)_2N{-}C(S)SSC(S)N(CH_3)_2 + H_2S^* \rightleftharpoons (CH_3)_2NC(=S)S^- + 2H^+ + (S^*)$$

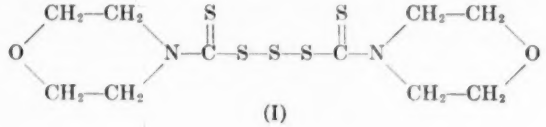
$$8(S^*) \longrightarrow S_8^*$$

$$2(CH_3)_2NC(S)C^- + 2H^+ \rightleftharpoons 2(CH_3)_2NC(S)SH \rightleftharpoons (CH_3)_2NC(S)SNH_2(CH_3)_2 + CS_2$$

the polymerization of S* atoms to S_8^* molecules. In the presence of insufficient H_2S^* and at a higher temperature, the S_8^* is known to undergo interchange with the sulfur in the TMTD[10] presumably by way of TMTT (reaction II) and higher sulfides.

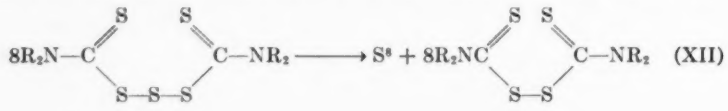
In collaboration with John Born, we have shown that H_2S^* initiation at 60° of TMTD-ZnO vulcanization results in the formation of nearly inactive ZnDMDC and a vulcanizate having (after ZnDMDC removal[10]) nearly all of the radioactivity of the H_2S^* started with. This is the expected result if vulcanization is a copolymerization of rubber molecules and sulfur radicals and is worthy of further study.

Since it was not possible to isolate TMTT for direct study[11] in vulcanization we have turned to the examination of di(morpholinyl-*N*-thiocarbamyl) trisulfide (I). Blake[12] reported the synthesis of this extraordinarily stable tri-



(I)

sulfide by the "amine-catalyzed" reaction of CS_2 with either morpholine monosulfide or the corresponding disulfide. The reaction of the disulfide also formed free sulfur. We can now report that sulfur has a stabilizing influence on (I). Thus, the preparation of (I) from morpholine monosulfide was conducted in the presence of sulfur and the product purified merely by extraction with CS_2, thereby avoiding decomposition as a result of heating, *e.g.*, with benzene. The melting point of the (I) which resulted was found to be 171–172° (dec.) (calculated for $C_{10}H_{16}O_2N_2S_5$: C 33.67, H 4.52, S 44.98; found: C 33.43, H 4.60, S 44.10). Blake reported 152–153° for a benzene-recrystallized product. Samples melting in this range have been found to contain the disulfide and sulfur presumably formed by the disproportionation XII. The

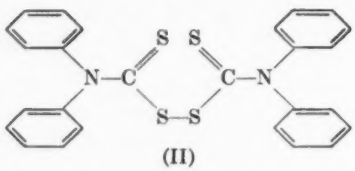


(I)

$R_2 = CH_2CH_2OCH_2CH_2$

disulfide was prepared from morpholinium *N*-morpholinyl carbodithioate by oxidation with $K_2S_2O_8$ in the usual way, and was found to melt at 149–150° (dec.) (calculated for $C_{10}H_{16}O_2N_2S_4$: C 37.00, H 4.97; found: C 37.29, H 4.99). Carter[13] reported this compound to melt at 135°. It and the trisulfide are vulcanizing agents as well as accelerators. As accelerators they display greater delayed action than TMTD. The disulfide is somewhat less active than TMTD. This behavior is believed to reflect the greater stability of (I) over TMTT and to be compatible with the idea that the vulcanizing action of a thiuram trisulfide, when suitably buffered, results from the liberation of mono or disulfur radicals directly or by reaction with H_2S.

With respect to stability, tetraphenylthiuram disulfide (II), m.p. 246° (dec.),



(II)

is notable because it displays almost no vulcanizing activity at ordinary curing temperatures. Fry and Farquhar[14] reported that (II) resulted in 20 per cent yield from the reaction of diphenylamine, carbon disulfide, and iodine in pyridine solution during a period of 10 weeks at room temperature. They seem to have been unaware of an earlier synthesis by one of us[15], which involved oxidation of sodium diphenyldithiocarbamate by iodine. Purification by alternate extraction with aqueous alcohol and benzene results in a purer product than that obtained by recrystallization (Calculated for $C_{26}H_{20}N_2S_4$: C 63.88, H 4.14; found: C 63.53, H 4.14.) The acid in this series, diphenyldithiocarbamic acid, results by acidifying an aqueous solution of the sodium salt. Unlike other dithiocarbamic acids, it is sufficiently stable to be crystallized from benzene (m.p. 147° (dec.); calculated for $C_{13}H_{11}NS_2$: C 63.62; H 4.53; found: C 63.97, H 4.45).

The stability of (II) is no doubt due in part to resonance effects, but by

comparison to TMTD, a hydrogen-rich compound, may well be connected also with the lack of available hydrogen for H_2S formation. Another compound whose very feeble vulcanizing action can be explained on the basis of stability is 2-benzothiazyl disulfide[16]. The action of this compound as an activator (replacement of ZnO) was recently ascribed[17] to its oxidizing action on rubber thiol groups and the rubber hydrocarbon. Its more or less reversible reactivity toward H_2S has been reported. Bedford and Gray[6] thought TMTD to be a replacement for ZnO. Fisher[18] proposed oxidation as a main reaction in vulcanization.

The varying ability of variously substituted thiocarbamyl groups to terminate sulfur chains, at least the short ones of interest in vulcanization, and the effect of H_2S on this property, suggest immediately that sulfur itself can be examined with respect to its behavior toward H_2S.

THE BEHAVIOR OF SULFUR TOWARD H_2S

Sulfur has recently been the object of several remarkable researches either by, or instigated by, Fanelli[18]. It is believed that these constitute the basis for a better understanding of vulcanization, including that with TMTD.

Bacon and Fanelli[20] were able to explain the peculiar viscosity-temperature curve for sulfur. Sulfur exhibits a maximum viscosity at 186–188°. For pure sulfur obtained by refluxing over MgO, they found a maximum viscosity of 932 poises; moreover the entire curve between 125° and 440° could be duplicated with decreasing temperature as well as with increasing temperature. They found that carbonaceous material, a common impurity in ordinary sulfur, leads to H_2S formation. Whereas ring opening of pure S_8 provided fragments that polymerized to give viscous sulfur, it was found that H_2S provided suitable end groups for modifying the polymer, thus resulting in a low viscosity over the whole liquid sulfur temperature range. A study by Fanelli[21] of the solubility of H_2S in sulfur over this same range confirmed this interpretation, since it was found that the solubility increased with temperature to a broad maximum. As the boiling point of sulfur was approached, the solubility fell to nothing. When sulfur saturated with H_2S, say at a high temperature, was cooled to lower temperatures, H_2S was evolved rather slowly as a result of the formation of S_8 rings, *i.e.*, ordinary sulfur. Fanelli[22] reported that his study of the surface tension of sulfur indicates that the average molecular complexity corresponds to S_7 and not to S_6 as had formerly been supposed. He doubts the existence of S_6 as a stable molecule. Fanelli has shown that the behavior of vapor, liquid, and crystalline sulfur can be explained largely on the basis of S_8 rings and their reversible conversion to sulfur chains[23] of various lengths suitably terminated with various groups such as halogen or hydrogen atoms. This work suggests that chain termination with various substances, especially hydrogen sulfide, is of the utmost significance in vulcanization.

In a study to be reported elsewhere, David Lawler from our laboratory finds the main peak in the mass spectrum of sulfur vapor to be the mass 64 peak, *i.e.*, the one corresponding to S_2.

Scott[24] recently reported sulfur vapor above 500° to be paramagnetic. This is in accord with a diradical nature for S_2 molecules and, together with Lawler's finding and the behavior of H_2S with various sulfides and sulfur, indicates the importance of looking for effects that could be due to radical intermediates such as $\cdot SS\cdot$ in vulcanization. The hydrogen sulfide initiation of TMTD vulcanization and the Peachey method of vulcanization, utilizing H_2S and SO_2, have been studied with this in mind and will now be reported.

HYDROGEN SULFIDE INITIATION OF TMTD VULCANIZATION

A technique found useful here has been to study the vulcanization of rubber cements in screw-capped vials or crown-capped bottles. These are sealed with suitable puncture-sealing gaskets[25] in order to permit the introduction of various gases and the withdrawal of air. The effects of H_2S on TMTD vulcanization reported here were observed at 70° for a cement compounded from 10 parts of milled crepe rubber in 100 parts of heptane. Prior to mixing with the solvent, 4 PHR of TMTD and 5 PHR of ZnO were added to the rubber on the mill.

In each test 5.0 cc. of the cement (containing about 0.4 gram of rubber, 0.016 gram of TMTD, and 0.02 gram of ZnO) was added to a 12 cc. vial. The vial was then capped and the air replaced by repeated evacuation and filling with high-purity N_2 and finally filling with N_2 at slightly more than one atmosphere pressure. The following statements summarize our findings.

(1) When the ZnO was omitted, there was no vulcanization, *i.e.*, no change in viscosity with any concentration of H_2S.

(2) When either 0.6 cc. or 1.8 cc. of H_2S was added to each vial, gelling occurred; but with 0.2 cc. or 5.4 cc. or no H_2S, the cements did not even thicken.

(3) Extracted rubber (presumably containing peroxides) gelled less readily than was the case with unextracted rubber cements. PBNA frequently overcame this effect, and some samples which had failed to gel with a given amount of H_2S did so on addition of the antioxidant. The addition of one PHR of PBNA to unextracted rubber on the mill permitted the preparation of a cement which gelled with a slightly lower concentration of H_2S than that required for a PBNA-free cement.

(4) Air, usually but not always, was inhibitory.

(5) Cumene hydroperoxides (1 PHR) enhanced gelling in most cases. In the presence of air and absence of PBNA, it was inhibitory.

(6) In one series of tests 0.6 cc. of H_2S produced gelling in the presence of 1 PHR of PBNA, 1 PHR of cumene hydroperoxide, and air, but failed to do so when any one of these three components was omitted. If all three were omitted, gelling occurred.

(7) Sulfur (1 PHR) greatly enhanced gelling; TMTD in this experiment obviously acted as an accelerator.

(8) Styrene, TMTM, and dodecanethiol were inhibitory. The effect of TMTM could be overcome by increasing the H_2S concentration, but this was not true with the effects of the other two.

(9) Diethylamine had no effect on gelling tendency in the presence of H_2S.

The effects of zinc oxide, H_2S, TMTM, and sulfur are those to be expected from previous experience. Especially they are in agreement with the work of Bedford and Gray[6] and Booth and Beaver[26] with respect to H_2S. The other effects except for that of PBNA will be treated in a later section.

The effect of PBNA on vulcanization established here is worthy of special note, since this substance is usually considered to be too weak a base to be an accelerator or even to be too weak to activate the thiazole type of acceleration. For a long time, however, in the testing of age-resisters, it had been noted that the original properties of cured age resister-free "black" stocks containing channel black were variable and were more variable than the controls containing PBNA. A recent study has shown that this antioxidant can have a significant effect on vulcanization. Thus tensile strength often is increased,

with little or no effect on the rate of vulcanization. This is shown by the tensile data presented in Table II for one such stock. The effect could not be detected in the press vulcanization of high-gum stocks and, therefore, may be related to Thornhill and Smith's observation[27] that channel black profoundly affects vulcanization.

TABLE II

EFFECT OF PBNA CONCENTRATION ON TENSILE STRENGTH OF EPC TREAD-TYPE STOCK

Base Recipe: rubber 100.0, EPC 50.0 ZnO 5.0, stearic acid 3.0, sulfur 3.0, MBTS[f] 1.0

	PBNA[b]											
	0.0			0.1			0.2			0.4		
Time[a]	M[c]	T[d]	E[e]	M	T	E	M	T	E	M	T	E
45	1610	3840	550	1650	3870	550	1650	3870	540	1610	3860	550
60	1880	3680	500	1930	3900	510	1950	3790	500	1820	3970	520

	PBNA[b]								
	0.8			1.6			3.2		
Time[a]	M	T	E	M	T	E	M	T	E
45	1770	3680	560	1570	4020	570	1690	4040	560
60	1920	4050	520	1810	4200	550	1700	4100	570

[a] Cure in minutes at 280° F.
[b] PBNA concentration in PHR.
[c] 300% modulus in lb. per sq. in.
[d] Tensile strength in lb. per sq. in.
[e] Per cent elongation in break.
[f] Benzothiazolyl disulfide.

THE HYDROGEN SULFIDE—SULFUR DIOXIDE VULCANIZATION OF CEMENTS

The Peachey method of vulcanization is especially adaptable to the puncture-sealing syringe technique. Using it, a number of observations have been made on the vulcanization of a 10 part rubber—100 part heptane cement. In each test, 5 cc. of the cement (containing about 0.4 gram of rubber) was introduced into a 12 cc. vial. The air was replaced with high-purity nitrogen and then one or more cycles consisting of 0.6 cc. of H_2S and an equal volume of SO_2, both gases measured at atmospheric pressure. After the introduction of each gas, the vial was shaken quickly and allowed to stand at room temperature from one to twenty-four hours.

The following statements summarize our findings.

(1) Zinc oxide, as might be expected, since it reacts readily with both gases, was strongly inhibitory. In its presence more cycles were required for vulcanization.

(2) Thinning always preceded gelling. This behavior could not be observed in the H_2S-initiated TMTD vulcanization of cements, and presumably is similar to the oxidative thinning of cements in the presence of H_2S or thiols that has been reported previously.

(3) An excess of H_2S over that required for reaction XIII was inhibitory and usually caused thinning of the cement.

(4) This type of vulcanization occurred better at 25° than at 50° and failed to occur at 70°, even with 5.4 cc. of each gas. It thus shows a "ceiling" temperature effect. At the higher temperature thinning of the cement occurred.

(5) Sulfur was an effective inhibitor. The effect may well be related to the

observation of Bacon and Fanelli[28] that sulfur can stabilize hydrogen polysulfides.

(6) Vulcanization occurred as readily in the dark as in the light of the laboratory.

(7) Dodecanethiol was a potent inhibitor. No combination of the thiol and SO_2 that was tried caused vulcanization.

(8) Hydrogen sulfide alone or SO_2 alone had no effect on the cement viscosity at 25°.

(9) Phenyl-β-naphthylamine, in contrast to its occasional beneficial effects in sulfur and TMTD vulcanization, had no effect, but cumene hydroperoxide enchanced vulcanization. The hydroperoxide also overcame the inhibiting effect of dodecanethiol.

(10) A minimum of 1.2 cc. of each gas, *i.e.*, two cycles, was required in the absence of other additive.

It may be noted from reactions I and XIII that TMTD and SO_2 have a common action toward H_2S, *i.e.*, an oxidizing action, and that in neither case is a depolymerization necessary to form S_2 as is the case with elementary sulfur, S_8. Hock and Schmidt[29] made the interesting observation that the dry gases

$$SO_2 + 2H_2S \longrightarrow 3(S) + 2H_2O \qquad \text{(XIII)}$$

do not react. Evidently the reaction is autocatalytic for in the presence of water free sulfur S_8 is formed.

DISCUSSION

Many of the effects noted here and elsewhere in vulcanization studies have to do with the presence of light, S_8, H_2S, thiols, oxidizing agents, peroxides, antioxidants, and oxygen. All may be potent sources of radicals under vulcanization conditions. It seems likely therefore that vulcanization, which involves the α-methylenic hydrogen atoms and also the double bonds of the rubber molecule, is radical initiated. The substances mentioned often affect each other and, in addition, may be sensitive to the polar effects of acids, bases, salts, and oxides.

The property of displaying an induction period, during which an inhibitor is consumed and following which the reaction of interest occurs, is often held as evidence for a radical reaction. This is especially true if the inhibitor is itself a radical or if it customarily reacts through radical formation. On the other hand, if the process under study occurs more readily in the presence of certain radicals or radical forming reagents it can be said to be initiated by these units, and further evidence of radical nature is scarcely required. It seems important to recognize that in a radical noncatalytic process, the inhibitor as well as the initiator is consumed, for then this type of process can be distinguished from a catalytic one in which the accessory material, the catalyst, is not used up. This, in no sense, argues against a catalyst functioning through the formation of radicals. Frequently, catalysts appear to act that way.

Vulcanization seems to be the type of noncatalytic process which, in the sense of the above discussion, requires initiation. We are of the opinion that the initiator is H_2S, which through oxidation forms sulfur radicals. Hydrogen sulfide occupies a novel position for at higher concentrations it can act as an inhibitor. Such an interpretation is attractive, for at once it supplies an explanation of the self-limiting effects of the process, at least some of which are

well known but poorly understood. These effects may be classified in various ways. We shall consider briefly (1) ceiling temperature effects and (2) the delayed action of certain systems.

Grenness[30] recently reported that zinc pentamethylenedithiocarbamate is active as an accelerator in the absence as well as in the presence of ZnO at room temperature. Contrary to its behavior in the presence of ZnO, it was inactive at temperatures of 130° and above when ZnO was not present. Similar effects were noted for ZnDMDC by Bedford and Gray, who explained them as being due to H_2S liberating the unstable dimethyl dithiocarbamic acid. The latter workers also pointed out the post-vulcanization problem. Thus a stock originally containing 2 PHR of sulfur 0.2 PHR of ZNDMDC and 5 PHR of ZnO was found to be fully cured in thirty minutes at 230° F, yet during seventy-five days at room temperature the cured samples underwent pronounced further vulcanization. Clearly this observation and that of Grenness are ceiling temperature effects. One is observed in the absence and the other in the presence of ZnO.

Recently Judeinstein[31] examined post-vulcanization as a feature of aging in a conventional 2-mercaptobenzothiazole accelerated stock His work is rather detailed and demonstrated that post-vulcanization at 70–80° is extensive especially for undercured specimens. In the presence of ZnO at the normal curing temperatures, it would be expected that the ZnO surface would be converted to ZnS, more or less impervious to H_2S. Since ZnS is a poor buffer for H_2S, the concentration of this component increases to a point which may be assumed to coincide with the stoppage of vulcanization.

Another instance of a ceiling temperature that of the Peachey cure, is described in the present paper. Reine[32] may have known of this sort of behavior, for he stated that the Peachey cure was ineffective at 140°. The ceiling temperature under our conditions was about 50°.

A plausible explanation of the ceiling temperatures thus far described rests on the assumptions (1) that the process involves a copolymerization of sulfur radicals with the double bonds of the rubber molecule; (2) that the H_2S formation process, which may involve one or more simultaneous and (or) consecutive reactions in addition to a simple reaction of sulfur radicals with α-methylenic hydrogen, has a steeper temperature coefficient of rate than the copolymerization reaction; (3) that the copolymerization reaction is initiated by the oxidation of small concentrations of H_2S and terminated by high concentrations, and (4) in the case of ZnO containing stocks, that the metallic oxide tends to become coated with ZnS, which is more or less impervious, so that the H_2S buffering capacity of the system is reduced.

Dainton and Ivin[33] have proposed recently that ceiling temperatures are typical of both radical and polar polymerization processes. The falling off in rate is to be expected as a result of the reversal of the propagation reaction as the temperature is increased. It is of interest that their work was based in considerable measure on the monoölefin-SO_2 copolymerization of Snow and Frey[34], a reaction that has some of the features of the Peachey cure, *e.g.*, it is inhibited by thiols and it occurs in the same temperature range. Van Amerongen[35], since our studies were completed, has reported that rubber and SO_2 react below but not above about 30°.

The proposal that ceiling temperatures in vulcanization are due primarily to the existence of two essential reactions in the process, which have different temperature coefficients, thus resembles the mechanism of Dainton and Ivin[33] for the self-limiting feature in their polymerizations. An essential difference

lies in the fact that a reversal of the chain propagation step in polymerization at the ceiling temperature does not seem to be involved in the case of vulcanization but rather chain termination.

The well-authenticated ceiling temperature effect in the polymerization of sulfur itself has been studied by Fanelli and coworkers[36], by Powell and Eyring[37], and by others, and has been mentioned previously in this report.

The delayed action period for accelerated stocks is of obvious interest with respect to self limiting effects. The length of the period for a given stock according to Shearer, Juve, and Musch[38], approximately doubles for a reduction in temperature of 10° C; likewise the cure rate similarly shows a temperature coefficient of about 2. It is thus possible to estimate within the normal curing range the overall time required for an "equivalent cure" with a minimum amount of preliminary data on cure rate.

The delayed action of TMTD vulcanization is sufficient so that an extracted rubber stock originally containing 4 PHR of TMTD and 5 of ZNO failed to display any sign of vulcanization during three years and three months at 25°. Data have shown[39] that a stock containing 3 PHR of TMTD and 5 PHR of ZnO when cured at 104.4°, 125.7°, and 141.7° C required 150, 15.5, and 5.5 minutes, respectively, for the tensile to reach 1800 p.si. if 0.5 minute is allowed for the specimen to reach the impressed temperature. Then, in accord with the Arrhenius equation, if these times are plotted on the log scale of semilog paper against the reciprocal of the absolute temperature, it is found that they fall on a straight line. Extrapolation of this line to the reciprocal of room temperature absolute (298.7°) gives a cure time of about 19 years (10^7 minutes). It is thus not surprising that our stock containing 4 PHR of TMTD failed to cure in three years and three months. Short-path distillation[10] of the aged stock yielded 85 per cent of the TMTD originally compounded. Recompounding of the distilled stock with 4 PHR of TMTD and curing for 30 minutes at 140° produced a well-vulcanized specimen. The fairly high tensile strength of about 2000 lb. per sq. in. reflected the protective action of TMTD.

It is our belief that the delayed action of accelerators is due to their ability in contact with ZnO to absorb H_2S which arises from the reaction of sulfur radicals with the active hydrogen of the rubber. For benzothiazolyl disulfide (reactions with ZnO are not shown) the reactions setting forth this principle are XIV, XV, and XVI in which R is benzothiazolyl. The number of sulfur atoms in these reactions is speculative. Langenbeck and Rheim[40] reported that the disulfide reacts on fusion with sulfur and suggested that sulfur chains

$$\text{R—SS—R} + \text{H}_2\text{S} \longrightarrow 2\text{RSH} + (\text{S}) \qquad \text{(XIV)}$$

$$\text{R—SS—R} + (\text{S}) \rightleftharpoons \text{RSSSR} \qquad \text{(XIVa)}$$

$$\text{RSSR} + \tfrac{1}{8}(\text{S}_8) \rightleftharpoons \text{RSSSR} \qquad \text{(XV)}$$

$$\text{RSSSR} + \text{H}_2\text{S} \rightleftharpoons 2\text{RSH} + (\text{S}_2) \qquad \text{(XVI)}$$

containing up to 80 sulfur atoms may be formed. Throdahl[41] reported recently that such mixtures, as might be expected, are more scorchy and more active than the disulfide and sulfur added separately. Reactions such as I, IV, XIV, and XVI suggest that the stability of the various sulfides toward sulfur and H_2S should determine the amount and concentration level of H_2S required for vulcanization.

This view is supported by the fact that various vulcanization systems ap-

parently require different levels of H_2S concentration, such as that existing in the absence (or the presence) of fatty acids. Thus TMTD vulcanization does not require fatty acids, but benzothiazolyl disulfide acceleration does. Hydrogen sulfide is known to reduce the latter disulfide (reaction XIV), but presumably less readily than it does TMTD. Reactions I and XIV are analogous. If R is a group which stabilizes the disulfide toward H_2S, it may be assumed that the corresponding trisulfide would be stable as compared to TMTT and, hence, the reaction of sulfur radicals with RSSR to form RSSSR would be the likely reaction.

Petrov's study[42] of benzothiazolyl disulfide acceleration is especially informative. He showed (1) that the monosulfide in the benzothiazolyl series forms the disulfide during vulcanization; (2) that the disulfide is reduced to the acid by H_2S (reaction XIV), with formation of sulfur, and (3) that the zinc salt reacts scarcely at all with sulfur to form the disulfide and ZnS. We wish to add reaction XIV to Petrov's mechanism and to suggest that the difficulty with which the zinc salt reacts with sulfur shows that this step has only incidental significance in vulcanization, the formation of a higher polysulfide probably being required.

Examination of the reactions in which sulfur radicals are liberated as the result of a polysulfide reacting with H_2S (*e.g.*, reaction XIV) shows that each case is an oxidation. Hence, the very excellent work of Barton[17] on certain oxidizing agents as activators instead of ZnO can be considered to support the present mechanism in that his reagents merely lower the concentration of H_2S by oxidation and, at the same time, supply sulfur radicals for polymerization.

Probably an excess of H_2S over the oxidizing agents would supply HS· radicals instead of ·S· or ·SS· radicals. This provides an approach to reversions, since H_2S as well as thiols (through RS· radicals) are known to initiate the oxidative degradation of rubber and since reversion occurs during the final stages of vulcanization, when the concentration of H_2S is likely to be high.

As a consequence of the essential absence of HS· radicals in the delayed action period, the reversion type of chain scission should not then occur. Of course, other types of degradation can and probably do occur during this period. As already noted PBNA counteracts one type. TMTD may counteract the same one.

The fact that the Arrhenius plot for the scorch period has the same slope as that for the cure period[38] strongly suggests that the controlling reaction (the slow step) is the same for both periods. The data presented in this series of papers suggest that this step is the H_2S formation reaction.

This leads to the final self-limiting effect to be discussed in this paper. This effect, in which the time of delayed action increases with increase in concentration of reagent, may be called the Jones-Depew effect[43], since they were the first to give a clear description of it. They reported that the time of delayed action for TMTM increased with increasing concentration of accelerator. Thus, 0.5 PHR showed less delayed action than 2.0 PHR. They happened to use ZnO containing lead oxide for activation. Our explanation for the effect is that TMTM in the presence of ZnO and PbO is so efficient for absorbing H_2S that not enough is available for the formation of sulfur radicals until the buffering capacity has been partly inactivated. Several other observations of this effect have been noticed, notably that of Throdahl and Harmon[44] for morpholine disulfide as a vulcanizing agent. We have found that the Mooney scorch periods for tetraphenylthiuram disulfide and dimorpholinyl-*N*-thiocarbamyl disulfide increase slightly with increase in con-

centration. It is known that the delayed action of benzothiazolyl disulfide does not increase with increase in concentration. This, no doubt, is to be correlated with the fact that the zinc salt in this series is less active than the disulfide or 2-mercaptobenzothiozole, whereas zinc dimethyldithiocarbamate is more active than TMTM or TMTD. Apparently, each system must be studied individually with respect to mechanism. With some, perhaps all, the delayed action period may overlap the initial period of cure. The degree of overlap might well explain the lack of increase in delayed action with increase in concentration of some accelerators. Much additional work is needed here.

In a subsequent paper it is hoped to deal with vulcanizate structure.

SYNOPSIS

Vulcanization with sulfur is ascribed to the formation of sulfur radicals, which are believed to copolymerize with the double bonds of the rubber molecule. Hydrogen sulfide is proposed as necessary for chain initiation, but, when formed in sufficient amounts, it serves as a chain terminator. This is believed to lead to numerous self-limiting features, including ceiling temperatures, post-vulcanization, and delayed-action effects. Initiation may result from the oxidation of H_2S to sulfur radicals, and termination to the formation of HS radicals.

REFERENCES

[1] Craig, Juve, and Davidson, *J. Polymer Sci.* **5**, 709 (1950).
[2] Five abbreviations are used throughout this paper: TMTM for tetramethylthiuram monosulfide; TMTD for tetramethylthiuram disulfide; TMTT for tetramethylthiuram trisulfide; ZnDMDC for zinc dimethyldithiocarbamate; TMTU for tetramethylthiourea; PBNA for phenyl-β-naphthylamine; and PHR for parts per hundred parts of rubber.
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CHANGES OF FATIGUE RESISTANCE OF VULCANIZED NATURAL RUBBERS DURING SWELLING *

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The penetration of a solvent into a polymer, with the ensuing development of a netlike structure, is accompanied by a change of molecular energy. Dogadkin and Gul showed that these changes of inter- and intramolecular energy are reflected in such properties of the vulcanizates as their fatigue resistance, relative elongation, tensile strength, etc. The absence of sufficiently complete and readily accessible data on the mechanism of rupture of vulcanizates under the influence of a static load, and their destruction through multiple deformation, excludes the possibility of a detailed discussion of the effect of swelling on these processes.

At the present time the work of Karmin, Einstein, Kuzminskiĭ, and Meisels describe the mechanism of swelling of rubbers sufficiently well so that it now appears possible and necessary to explain these processes in greater detail. In view of this, the swelling method was used as far as possible in the present work, in order to lengthen the life of specimens which are subjected to multiple deformation. By comparing the fatigue strength of vulcanizates swollen to varying degrees, we attempted to determine the possibility of increasing the fatigue resistance of specimens as a result of the increased size of the cross-section and decrease of the modulus of elasticity during swelling. In preceding works[1] the fatigue resistance of vulcanizates of varying degrees of swelling were compared at identical deformation amplitudes. In this case, on further swelling the test-specimens operate under more favorable conditions, because, when amplitudes of deformation are kept constant, the decrease of the modulus of elasticity is accompanied by a decrease of the work of deformation. As a result of this, the losses of mechanical energy, in particular that consumed in the activation of the chemical processes which cause destruction of the specimen (when the loss coefficients are equal), will be smaller in swollen rubbers.

It is particularly interesting to observe the influence of swelling on fatigue resistance with a constant deforming load. With this purpose in view, Gul built the machine shown in Figure 1.

This machine consists of a frame 1, subjected to reciprocating motion by a motor connected to a crank and connecting rod mechanism. The motor and the mechanism are installed along the frame and are mounted on a plate on which are mounted also the supports of the clamps 4 and the block 0. On the frame 1 are fastened the driving rods 2, with the clamps 3 at the ends. The driving rods are mounted at one end on a carriage which moves through the frame 1. Depending on how much the rods 2 are moved with respect to the immovable clamps 4 and the lower clamps 5, the amount of the working part of the rubber specimens 6 and 6′ changes. The upper part of the machine is heat-

* Translated for Rubber Chemistry and Technology by Alan Davis from *Kolloidnyi Zhurnal* 13, No. 5, pages 339–345 (1951).

controlled and, by such control experiments, a constant amplitude of deformation is possible. The lower part of the machine is used for testing the specimens with constant minimum deforming loads. A set of weights P, whose value can be changed within wide limits (depending on the modulus of the specimen) is attached to the lower clamps 5 by thin rods. On each rod is a projecting disc B, which contacts the bumper 0 when the rod is moved. During repeated stretching of the specimens, because of the periodic movement of the frame, and likewise of the clamps 3, upward and downward, the specimens are stretched when the frame ascends; the lower clamps touch the bumper 0 and the specimens are shortened when the frame descends. In the lower position of the mechanism the specimen 6′ is deformed only by the action of the weight of the lower clamps and the weights P. If, during repeated stretching, because of the

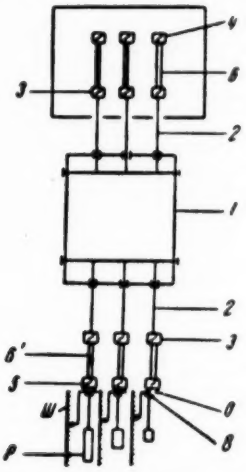

FIG. 1.—Diagram of mechanism for measuring the fatigue life of vulcanizates.

development of relaxation processes or the development of permanent processes of structural degradation, the length of the specimen increases, then in the lower position the part B extends beyond the bumper and these parts begin to knock. In such case the bumper 0 is moved down manually until the knocking ceases.

The movement of the bumper can easily be regulated. The bumpers are fastened with a vernier which moves along a scale W. Thus, it is possible to measure the length of the specimens during the fatigue process.

By means of a rheostat it is possible to change the rate of deformation between 200 and 400 cycles per minute.

In the present study, the testing of specimens for fatigue resistance was carried out at a constant minimum deforming load throughout the experiments. The specimens were first deformed 60 per cent. Vulcanizates of the following composition were experimentally tested:

Smoked sheet rubber	100 parts by weight
Sulfur	2
Tetramethylthiuram disulfide	0.2
Zinc oxide	1
Stearic acid	1

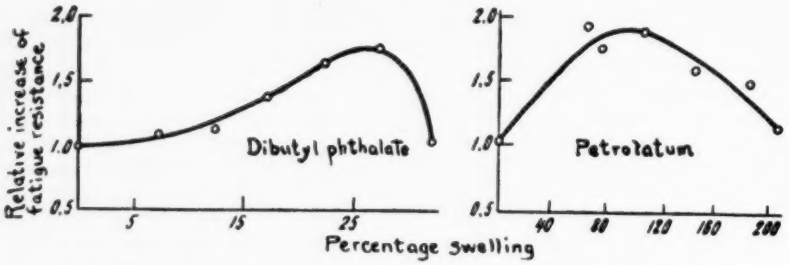

FIG. 2.—Change of fatigue resistance of natural-rubber vulcanizates with increase of their degree of swelling in dibutyl phthalate and in petrolatum.

The mixture was vulcanized in a press at 142° for 10 minutes.

The specimens were cut with a special die giving specimens 4 mm. wide, 1.0–1.5 mm. thick, and 50 mm. long.

As solvents for swelling the samples, refined petrolatum and dibutyl phthalate were chosen. The degree of swelling was determined by the weight method, and a minimum amount of solvent was used in order to decrease any leaching out of the compounding ingredients. The amplitudes of deformation selected ranged from 60 per cent up to 200 per cent. As a result of repeated deformations, the length of the specimen continually increased. Since experiments on the multiple deformation of vulcanizates are characterized by large deviations of the experimental data, in the present work the results obtained were treated statistically.

The values of relative fatigue resistance[2] of a vulcanizate swollen in dibutyl phthalate were determined experimentally. By arranging the results in order of degree of swelling, *i.e.*, 5–10 per cent, 10–15 per cent, 18–20 per cent, 25–30 per cent, 30–35 per cent, and statistically interpreting them, we obtained the

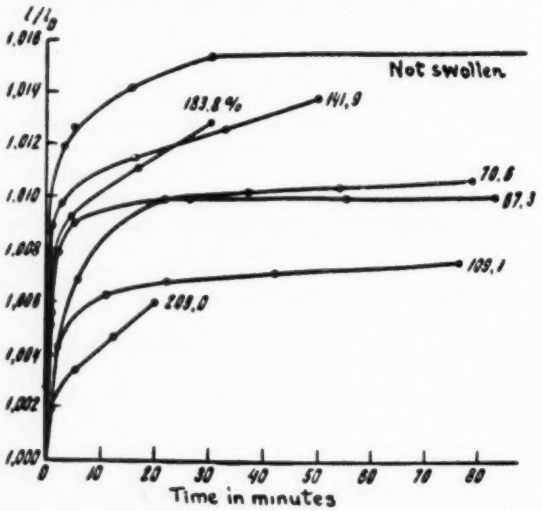

FIG. 3.—Progress of dynamic relaxation of vulcanizates of natural rubber swollen in petrolatum.

curve shown in Figure 2a. The corresponding relation for the case of swelling in petrolatum is shown in Figure 2b. As was already shown above, the specimens were stretched continually during the multiple deformation process. This phenomenon is analogous to the increase of length under the influence of a static load, which will later be called, as was done by Karmin and Epstein, dynamic relaxation.

Figures 3 and 4 show a few curves of the growth of dynamic relaxation of swollen specimens with time.

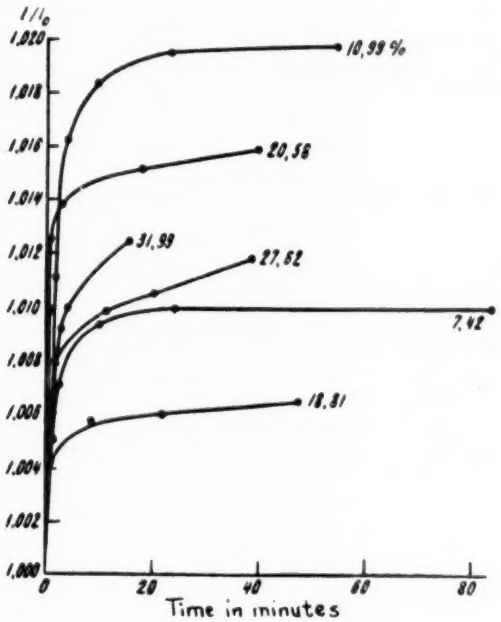

FIG. 4.—Development of dynamic relaxation in vulcanized natural rubber swollen in dibutyl phthalate.

The curve of dynamic relaxation can be divided into two parts. The first region of the curve represents the process of transition of the system into a mechanical equilibrium, and is distinguished from the processes which change the chemical structure of the polymer. The second part of the curve, which is essentially a straight line, is a measure of the intensity of penetration of the destructive processes.

The change of movement in the chain molecules can easily be traced by the change of time, in the course of which the curve of relative length-time of deformation becomes linear. We shall henceforth call this time interval the normal rate of relaxation. The change of movement of the chain molecules can easily be traced by the change of time, in the course of which the curve of relative length-time deformation becomes linear. We shall henceforth call this time interval the normal rate of relaxation. The change of movement of the chain molecules of vulcanized natural rubber as a function of the degree of swelling is shown in Figure 5. The value of the normal relaxation time is determined as the mean of several measurements with an accuracy of 5 minutes.

Stress-strain curves were recorded on a dynamometer. The stress was a function of the cross-section of the swollen specimens. The cross-sections of unswollen specimens were measured, and the cross-sections of the swollen specimens were calculated on the basis of the degree of swelling. The results are given in Figures 6a and 6b.

The data obtained permit a more detailed analysis of the mechanism of change of fatigue resistance during swelling of vulcanizates.

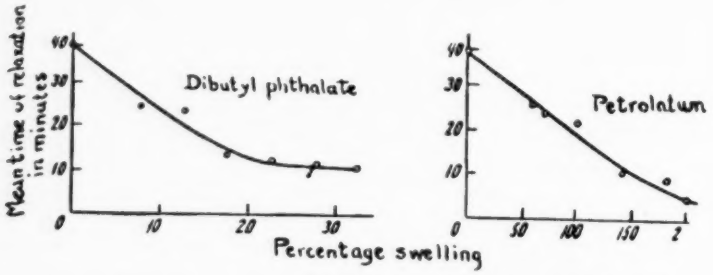

FIG. 5.—Change of movement of chain molecules of vulcanized natural rubber with respect to degree of swelling: (a) in dibutyl phthalate, (b) in petrolatum.

The first, and it seems, the principal cause of the increase of creep of vulcanizates when the degree of swelling is increased is the decrease of energy loss during multiple deformation. During swelling, with resulting increased movement of the chain molecules, the energy losses decrease. Besides, the increased movement of the chain molecules causes a more rapid equalization of stress, which must in turn have a substantial influence on the formation and growth of primary centers of destruction. Decrease of stress in the specimen, because of the increased cross-sectional area, can, under certain conditions, cause a decrease of energy consumed during deformation of the specimen. In the cases studied, the increased cross-sectional area is not accompanied by a perceptible increase of the structural units which transmit the stress throughout

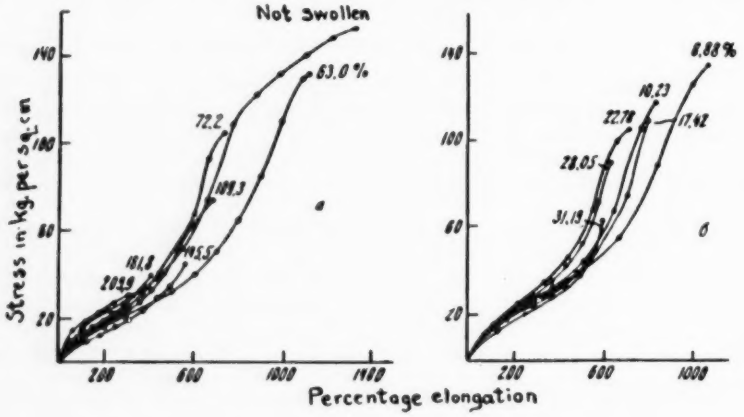

FIG. 6.—Stress-strain curves for vulcanized natural rubber of various degrees of swelling: (a) in petrolatum, (b) in dibutyl phthalate.

the specimen. For this reason, the change of size of the cross-section itself does not have any appreciable influence on fatigue resistance, since the load remains constant, but the amplitude of deformation increases with an increase of the degree of swelling.

As is shown, the specific energy of deformation can be measured as follows:

$$W_D = \int_{L_1}^{L_2} \sigma \, dL \tag{1}$$

where W_D is the quantity of energy lost during the deformation of 1 cc.; σ is the stress, and L is the elongation. Assuming that, during deformation, the behavior of swollen vulcanizates conforms to the equation proposed by Flory[3] for the case of deformation of 1 cc. of swollen rubber, we have:

$$W_D = \int_{L_1}^{L_2} \frac{RT\rho}{V^{\frac{1}{3}}M}\left(L - \frac{1}{L_1}\right) dL = \frac{RT\rho}{V^{\frac{1}{3}}2M}\left[L^2\right]_{L_1}^{L_2} - \frac{RT\rho}{V^{\frac{1}{3}}M}\left[\frac{1}{L}\right]_{L_1}^{L_2} \tag{2}$$

where V is the volume of polymer in the swollen gel; M is the molecular weight of the chain segments of the rubber molecules included within a spatial network; R is the gas constant, and T is the absolute temperature.

From this it follows that the increased degree of swelling must increase the amount of specific energy of deformation. In the case where the deforming load is maintained constant while V is simultaneously changed, L_1 and L_2 both increase. Increase of the values of L_1 and L_2, and also increase of the difference $L_2 - L_1$, which is shown by the curves, which are analogous to the curves in Figures 6a and 6b, must lead, with an increase of the degree of swelling, to an increase of specific energy of deformation. The relations studied are valid when a state of equilibrium exists.

In the fatiguing of rubber by repeated deformations, the decisive role belongs, not to the thermodynamics, but to the kinetics of high elastic deformation. Under these conditions the effect of the increase of L_1 and L_2 on the increase of the value of W_D is even more visible. Nevertheless, the large increase of fatigue resistance attests to the decrease of energy lost in the activation of the particular chemical processes which lead to destruction of the rubber. Since, in these experiments, measures were taken to prevent a decrease of the work of deformation, the decrease of energy loss would seem to be a result of the decrease of deformation energy lost as a result of activation of the chemical processes. These losses are possible in the form of kinetic energy of thermal movement, as well as in the form of heat transfer, as well as in the form of an accumulation of mechanical energy in the process of transfer of forces through the chain molecules on certain particles of the chains which are established as a result of the greater reactivity. An increase of kinetic energy of thermal movement of the links of the chain molecules and the local formation of particles with a greater reactivity, because of the so-called mechanical activation, is connected with the difficulties arising during the transfer of stress from one end of the deformed sample to the other. They will be smaller as the movement of the chain molecules is greater. The increase of motion of the chain molecules was measured by the relation of the relaxation time to the degree of swelling.

From Figure 5 it follows that the normal rate of relaxation decreases directly with an increase of the degree of swelling in the solvents used. This causes to a large degree a decrease of energy loss as the degree of swelling increases.

An examination of the stress-strain curves (Figures 6a and 6b) clearly shows the large decrease of tensile strength and decrease of relative elongation commensurate with the increase of degree of swelling. A decrease of the modulus of high elasticity with constant minimum deforming load, as was mentioned, is accompanied by an increase of the amplitude of deformation of the specimens. The difference between the values of multiple deformation and elongation at the moment of rupture decreases with an increase of the degree of swelling. With a certain correspondence between the elongation at the moment of rupture and the maximum value of deformation, destruction of the sample takes place. At a given rate of deformation, this relation is equal to approximately 3.0.

The description above is well illustrated by a comparison of the degree of swelling-fatigue resistance curves for dibutyl phthalate and petrolatum (Figures 2a and 2b). During swelling of vulcanized natural rubber in petrolatum (Figure 3), an increase of creep is observed up to a swelling of 90–100 per cent. The favorable influence of a decrease of energy loss is so strong here that it prevails over the influence of a decrease of relative elongation. Commencing at a swelling of 100 per cent, the relation of the maximum deformation and relative elongation approximates the critical value:

$$\frac{\text{maximum deformation}}{\text{relative elongation at moment of rupture}} \approx 3 \qquad (3)$$

When dibutyl phthalate is used as the solvent, a change of fatigue resistance with increase of the degree of swelling is observed in fewer cases than with petrolatum. To reach the maximum fatigue resistance, a much smaller degree of swelling is necessary than in the case of petrolatum (Figure 2a). This is explained by the fact that the presence of polar and nonpolar bridges in the dibutyl phthalate molecule creates conditions suitable to the induction and dispersion reactions between the solvent and links of the chain molecule. Apparently formation of hydrogen bonds also takes place. When dibutyl phthalate is added to a vulcanizate, conditions favorable to the exposure of all possible centers of intermolecular activity are created, *i.e.*, there is increased motion of the chain rubber molecules, with resulting decrease of energy loss. The relatively great effectiveness of dibutyl phthalate is attributable to the fact that the small swelling it causes in comparison to that caused by petrolatum results in a relatively small increase of volume and, consequently, to a smaller three-dimensional deformation of the chain molecules. A comparison of the graphs of the changes of fatigue resistance of vulcanized natural rubbers swollen in petrolatum and in dibutyl phthalate (see Figure 2) shows that the optimum increase of fatigue resistance is the same in each case. This is, of course, based on the assumption that, during swelling, the more effective solvent (in the sense of intermolecular activity) increases the fatigue resistance correspondingly more because of the decrease of energy loss, and also causes the ratio of the maximum deformation to the relative elongation at rupture to approach a critical value faster.

CONCLUSIONS

A method of fatiguing swollen vulcanizates of natural rubber while maintaining a minimum deforming load, independent of the change of modulus of elasticity of the experimental specimens, was devised.

The effect of swelling vulcanized natural rubber in petrolatum and in dibutyl phthalate on fatigue resistance was studied.

With increase of swelling of a vulcanizate in dibutyl phthalate and in petrolatum, an initial increase of fatigue resistance was observed up to 1.8 times the fatigue resistance of the unswollen vulcanizate. Following this, a decrease of fatigue resistance was observed.[1]

The equation obtained for the change of fatigue resistance as a function of the degree of swelling is explained by two simultaneous processes: (1) increase of fatigue resistance because of decrease of energy loss in the destructionof intermolecular bonds, and (2) initiation of chemical processes leading to destruction, and a smaller difference between the deformation and the relative elongation at rupture.

The effect of the character of the solvent used for swelling on the nature of the fatigue resistance-swelling relation is shown.

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THE EFFECT OF ELONGATION ON THE TIME OF RELAXATION T_2 OF NATURAL RUBBER *

ARMAND COHEN-HADRIA AND ROBERT GABILLARD

EXPERIMENTAL APPARATUS AND TECHNIQUE

Natural rubber vulcanized under controlled conditions[1] was used in the experiments, and the apparatus, which has been described elsewhere[2], was tuned to the proton resonance.

The test-specimen, of elongated form, was stretched by means of two clamps, which held it at opposite points of the coil of the oscillating circuit. At the same time it could be cooled by circulating liquid air.

The T_2 value of the sample was measured by means of a standard technique, *i.e.*, by the line width at low temperatures, and by means of a technique recently described[3], *i.e.*, measurement of the amplitude and of the exponential time constant of the decrease of the signal above $\theta \cong -15°$ C. The temperature was measured by a thermoelectric couple.

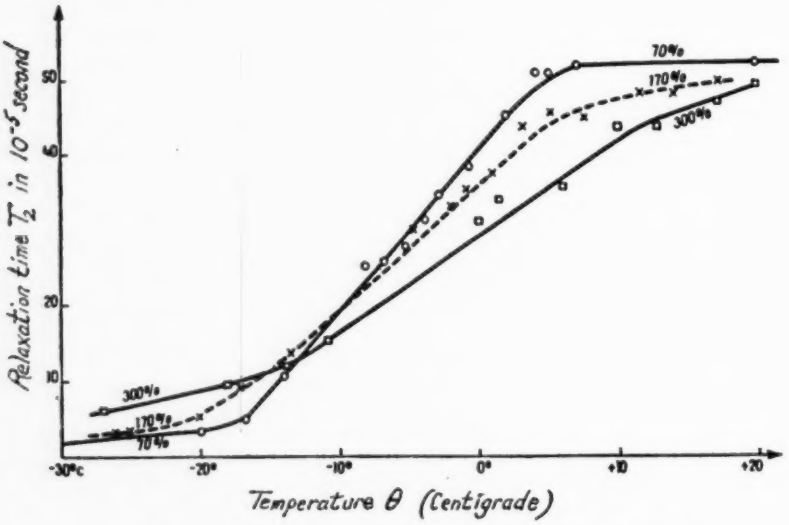

FIG. 1.—Relaxation time as a function of the temperature, $T_2 = f(\theta)$, for different elongations ($\Delta l/l$ = 70, 170, and 300 per cent).

$T_2 = f(\theta)$ curves were constructed for several degrees of elongation to which the rubber was subjected (see Figure 1).

Each sample for which a curve was constructed was of such a shape and size that its cross-section was always the same when the stress had once been ap-

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plied[4]. By this precaution, the degree of static inhomogeneity of the magnetic field remained constant through the whole range of measurements.

EXPERIMENTAL RESULTS

The $T_2 = f(\theta)$ curves which were obtained (see Figure 1) are characteristic of the transition already described by Holroyd, Codrington, Mrowca, and Guth[5].

At the temperature of the laboratory, the T_2 value of the particular rubber tested was close to 5×10^{-4} second, a value below the limit governed by the

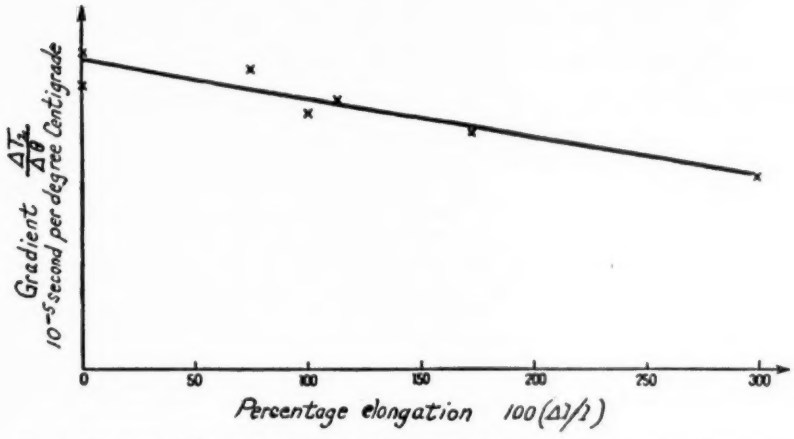

FIG. 2.—Gradient $\Delta T_2/\Delta\theta$ as a function of the elongation, $\Delta l/l$, in percentage, in the transition range.

inhomogeneity of the magnetic field, *viz.*, $T_2 = 8.5 \times 10^{-4}$ second. With rise of temperature, T_2 decreased rapidly to the point: $T_2 \cong 5 \times 10^{-5}$ second, in such a way that the relation was almost linear within the temperature range between $-5°$ and $-15°$ C. Beyond this transition zone, T_2 decreased very slowly down to the temperature of liquid air, and finally reached the value: T_2 (liquid air) $= 2 \times 10^{-5}$ second, below which no measurements were made.

The three curves in Figure 1 represent the relative elongations, $\Delta l/l$, of 70, 170, and 300 per cent, respectively. Two phenomena are indicated by these curves: (1) at laboratory temperature, the value of T_2 decreases slightly with increase of elongation, and (2) the gradient of the transition region decreases linearly as a function of the elongation (see Figure 2).

In an attempt to interpret these experimental results, we have taken into consideration the effect of a change of the relative magnitude of the intramolecular spin-spin interactions and spin-spin interactions between neighboring chains. However, we are withholding any further discussion of this theory for a subsequent paper. Meantime we believe it helpful to compare these results with results obtained by swelling natural crepe rubber in carbon tetrachloride. In the latter case, the swelling led to the following increases of the T_2 value:

T_2 (original crepe)	$6 \times 1;^{-4}$ second
T_2 (crepe swollen 25%)	8×10^{-4} second $\cong T_2{}^*$

SUMMARY

An experimental study, first, of the relaxation time T_2 of natural rubber as a function of temperature and, in turn, of the influence of elongation on these changes of T_2 has proved that, within the temperature range of $-15°$ and $5°$ C, the gradient $\Delta T_2/\Delta\theta$ of the $T_2 = f(\theta)$ curve decreases in proportion to the elongation.

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[4] By this, the author means that each test-specimen had its own specific dimensions, which were so chosen that, when the test-specimens were stretched to the different elongations being studied, the cross-section of each specimen was the same in every case. Thus, the original cross-section of the specimen to be elongated 170 per cent would be greater than that of the original cross-section of the specimen to be elongated only 70 per cent, and by proper calculation, the cross-sections of the two specimens were identical when the specimens were stretched 170 and 70 per cent, respectively [Editor].
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INVESTIGATION OF FRACTIONATED POLYBUTADIENES BY A DYNAMIC-OPTICAL METHOD *

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A number of studies of the dynamic double refraction of solutions of polymers[1] showed that studies of this kind can provide information on the number, shape, solidity, and optical properties of macromolecules.

In one of these studies[2] of fractionated samples of loaded polybutadiene, it was established that the results of investigations of unfractionated substances can be greatly distorted by polydispersion.

In the present work a number of fractions of unloaded polybutadiene rubbers, prepared under different conditions of polymerization, were studied by this method. The purpose of these studies was to explain the nature of the relation of the dynamic-optical properties of a polymer to its molecular weight and the influence of the solvent on the molecular structure of a polymer in solution. In addition, the attempt was made to determine to what degree the structural properties of a polymer, resulting from different conditions of polymerization, can be detected by the dynamic-optical method.

APPARATUS AND METHOD

Double refraction and its angle of orientation during flow were measured in a cylindrical apparatus with an internal rotor. The apparatus was constructed of chrome-plated brass, and was equipped with ball-bearings in the upper part (see Figure 1). It was surrounded by a water jacket, by which the temperature of the unit was kept constant. The space between the stator and the rotor was 0.1 mm. As materials for study, three samples of unloaded rubber were chosen, which had been polymerized at 20°, 40°, and 60° C. For the sake of brevity, these will be called, respectively, A, B, and C.

The samples were fractionated by the fractional precipitation method from benzene solutions with acetone. By this method, five or six fractions of progressively decreasing molecular weight were obtained from each sample. The molecular weights of the fractions were calculated from the viscosities of the solutions according to the formula obtained for these polymers by Zhukov, Poddubny and Lebedev[3]. The viscosities of each of the benzene solutions $[\eta]$, and the molecular weights calculated from them, μ, are given in Tables 1, 2, and 3.

Besides these viscosity measurements of dilute solutions, we also investigated the effect of the rate of flow of a solution in the capillary tube on its viscosity (structural viscosity) by the method used several times previously[4].

* Translated for Rubber Chemistry and Technology by Alan Davis from the *Journal of Physical Chemistry*, USSR, Vol. 24, No. 8, pages 994–1003, August 1950.

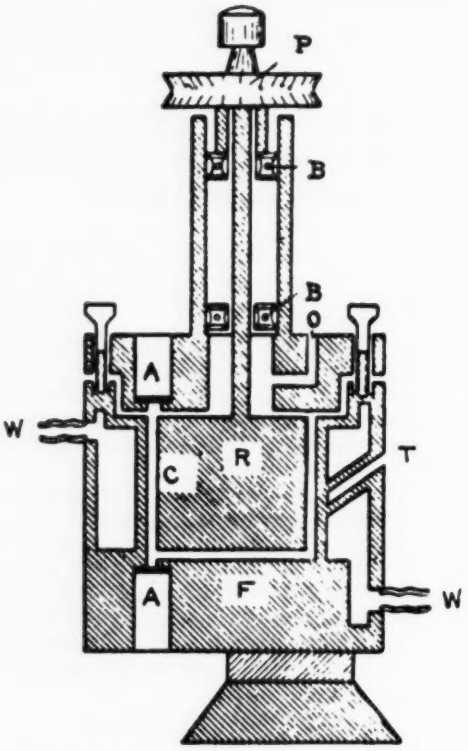

FIG. 1.—Diagram of the apparatus used in the dynamic-optical method.

A. Apperture
B. Ball-bearing
C. Clearance between rotor and frame
F. Frame
O. Opening for charging
P. Pulley
R. Rotor
T. Thermometer well
W. Inlet and outlet of water jacket

RESULTS OF VISCOSITY MEASUREMENTS

All the samples studied showed marked structure viscosity at sufficiently high concentrations. The η_r relation between the relative viscosity of solutions of certain fractions and the mean gradient of the rate of flow g through the capillary tube is shown in Figure 2.

For characterizing quantitatively the structure viscosity of a polymer, it is possible to use a method which had been used earlier in a study of polyisobutylene[5].

The relation between η_r and the difference of pressure p at the ends of the capillary can be expressed approximately by the equation:

$$\eta_r = A \left(\frac{p}{p_0} \right)^{\gamma} \tag{1}$$

TABLE 1

UNCOMPOUNDED POLYBUTADIENE, POLYMERIZED AT 20° C

Fraction	$[\eta]$	$\mu \cdot 10^{-3}$	Solvent	$C_v \cdot 10^2$	η_r	$X \cdot 10^3$	$X_w \cdot 10^3$	$W \cdot 10^{16}$
	3.945		Benzene	0.56	4.1	11.2		
				0.845	6.85	11.5	11.4	29.2
		555						
I			n = 1.501	1.27	10.3	11.6		
n = 1.51								
			Hexane	0.77	4.6	9.6		
				1.16	7.7	11.1	11.7	
			n = 1.396	1.74	15.0	12.3		
	2.99	378		0.76	4.77	7.35		
			Benzene	1.14	7.43	7.53	7.44	13.8
				1.52	12.9	7.45		
II				0.92	4.9	8.7		
			Hexane	1.38	8.48	8.2	8.51	
				2.07	16.7	8.65		
	1.951			1.13	4.56	4.72		
		210	Benzene	1.69	7.85	4.3	4.77	6.6
				2.25	12.9	5.3		
III				1.83	7.36	5.2	5.35	
			Hexane	2.76	14.9	5.5		

where p_0 is the small pressure difference, taken as a base, and A is a constant. The factor γ for values of p which exceed p_0 not more than 2 or 3 times is constant for a given solution, and therefore characterizes its structure viscosity.

The value of γ increases sharply with increase of the concentration of the solution. The latter is illustrated graphically in Figure 3. For any given concentration, the structural viscosity increases with increase of the molecular weight of the fraction.

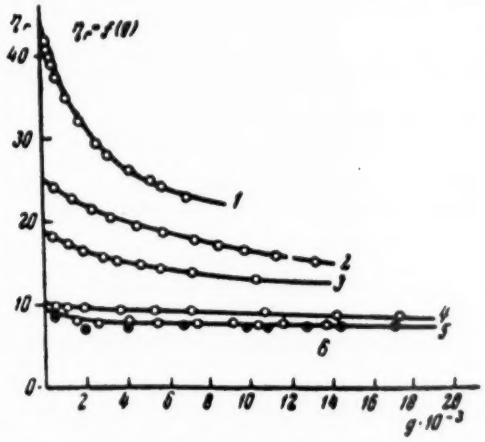

FIG. 2.—Relation between relative viscosity and rate of flow gradient of solutions of polybutadiene, prepared by polymerization at 20° C.

1, 2. Fraction I in benzene (1, C_v = 1.69% and in hexane (2, C_v = 1.74%).
3, 4. Fraction II in benzene (3, C_v = 1.52%) and in hexane (4, C_v = 1.38%).
5, 6. Fraction III in benzene (5 C_v = 1.69%) and in hexane (6, C_v = 1.87%).

TABLE 2

UNCOMPOUNDED POLYBUTADIENE, POLYMERIZED AT 40° C

Fraction	$[\eta]$	$\mu \cdot 10^{-3}$	Solvent	$C_v \cdot 10^2$	η_r	$X \cdot 10^3$	$X_w \cdot 10^3$	$W \cdot 10^{16}$
	3.356		Benzene	1.3	11.6	10.1		
I		443					9.9	14.6
$n = 1.51$			$n = 1.501$	0.86	6.3	9.7		
			Hexane $n = 1.396$	1.18	7.0	12.0	12.0	
	2.723		Benzene	1.47	9.75	7.1	7.1	6.9
			Hexane	1.08	4.9	8.1	8.1	
	1.789			1.87	10.0	4.62		
		219	Benzene	2.5	15.86	5.61	5.1	
III			Hexane	1.95	6.52	5.9		
				2.92	15.7	4.8	5.37	
				2.4	7.56	2.99		
	1.344		Benzene	3.6	15.2	3.18	3.09	2.48
IV		125						
			Hexane	2.96	9.3	3.36	3.36	

Comparison of the $\gamma = \gamma(C_v)$ curves for solutions and various solvents leads to characteristic results. For the same fraction in benzene solutions, the structure viscosity is much greater than in hexane solutions, since the nature of the structure viscosity is not governed primarily by the orientation of the polymer molecules in flow, but by the destruction of the "structure" caused by their interaction[6], the observed decrease of γ during solution in hexane by comparison with benzene solution must be considered an indication of the smaller size of the polymer molecules in hexane.

This means that a polybutadiene molecule in hexane has a more compact structure (a spherical particle with a higher degree of convolution), than in benzene solution.

This is attested also by the fact that the values of the relative viscosity η_r in hexane are smaller than in benzene (see Figure 2 and Tables 1, 2, and 3).

EFFECT OF SOLVENT ON THE DYNAMIC-OPTICAL PROPERTIES OF POLYMER

The conclusions, analogous to the results of the preceding paragraph, are reached by a study of double refraction in various solvents.

TABLE 3

UNCOMPOUNDED POLYBUTADIENE, POLYMERIZED AT 60° C

Fraction	$[\eta]$	$\mu \cdot 10^{-3}$	Solvent	$C_v \cdot 10^2$	η_r	$X \cdot 10^3$	$X_w \cdot 10^3$
	2.622		Benzene	1.16	6.86	5.76	
I							6.0
$n = 1.501$		315	$n = 1.501$	0.78	4.1	6.25	
			Hexane	1.6	7.8	8.36	
							8.68
			$n = 1.396$	1.07	4.6	9.0	
II	1.906		Benzene	1.52	5.3	4.4	4.4
		203	Hexane	1.49	4.6	6.8	6.8
	0.7468		Benzene	3.54	7.2	1.97	1.97
III		56	Hexane	3.0	4.5	2.38	2.38

The dynamic-optical constant X, determined by the following equation, serves as a measure of double refraction:

$$X = \lim_{\substack{g \to 0 \\ c \to 0}} \left(\frac{\Delta n}{g \eta C_v} \right) \cong \lim_{g \to 0} \left(\frac{\Delta n}{g \cdot C_v \cdot \eta_0 \sqrt{\eta_r}} \right) \qquad (2)$$

where Δn is the difference between the principal two refractive indexes of the solvent at a rate gradient, g, and η and η_0 are the absolute viscosities of solution and of the pure solvent, respectively.

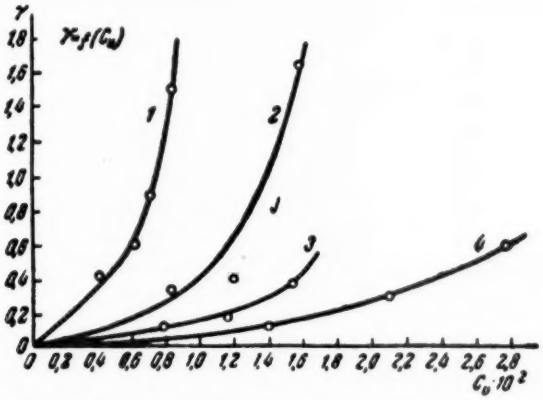

FIG. 3.—Structure viscosity of a solution as a function of its concentration. Polybutadiene prepared by polymerization at 20° C.

1. Fraction I in benzene
2. Fraction II in hexane
3. Fraction III in benzene
4. Fraction III in hexane

As was shown in a number of works[4], the quantity X to a large degree depends on the difference between the refractive indexes of the solvent n_0 and of the dissolved polymer n (effect of shape), while the curve $X = f(n_0^2)$ has a parabolic form, with a minimum at the point $n = n_0$, where the double refraction consists entirely of the photoelastic effect X_0.

When this relationship is "normal," for a solvent in which n_0 differs from n by 0.1, the value of X usually exceeds X_0 by 3 to 3.5 times[7].

The values of the dynamic-optical constants X, derived for various polybutadiene fractions ($n = 1.50$) in benzene ($n = 1.501$) and hexane ($n = 1.396$) solutions, are shown in Tables 1, 2, and 3. We see that, at a difference of $n_0 - n \approx 0.1$ in hexane solutions, the value of X slightly exceeds the value in benzene (X_0), while for specimen A this excess is no more than 10 per cent, for specimen B about 10–20 per cent, and for specimen C $\approx$ 25–40 per cent.

Since the value of X is directly dependent on the size of the macromolecule in solution, the much smaller value for hexane solutions must be considered an indication that, in hexane solutions, the polybutadiene molecule has a more convoluted form than in benzene.

This "structural" influence of the solvent is observed to a high degree in solvents polymerized at a relatively low temperature (specimen A).

Another characteristic of the mechanical properties and shape of the molecule in solution is the course of the curve $\Delta n = f(g)$[8].

In fact, if the globular molecule is undergoing laminar flow, it revolves at an angular rate which is determined by its geometric dimensions and the value of the gradient g. Besides, it also undergoes periodic extensions and compressions (once during the period of revolution), which are responsible for the photoelastic phase of double refraction.

If a molecular chain possesses sufficient flexibility, that is, can easily be bent and easily change its shape, then in the periodic field of force it will "roll up" and "unroll" in phase with the force acting upon it. Here the amplitude of these deformations increases in very close proportion to g. In a solution containing such molecules, the double refraction sharply increases with the rate

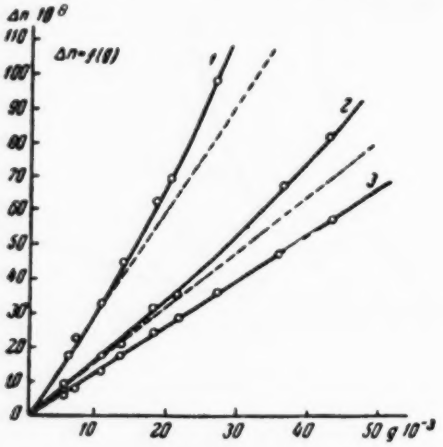

FIG. 4.—Uncompounded polybutadiene, prepared by polymerization at 20° C, in benzene.

1. Fraction I $C_v = 1.27\%$; $\eta_r = 10.3$
2. Fraction II $C_v = 1.14\%$; $\eta_r = 7.43$
3. Fraction III $C_v = 1.69\%$; $\eta_r = 7.85$

gradient, and the $\Delta n = f(g)$ relation is expressed by a curve whose top portion is concave. This relation was determined experimentally for the majority of the polymers investigated hitherto. It appears especially infrequently in high-molecular substances with linear unbranched molecules: in natural rubber[9], polyisobutylene[6], and polystyrene[10].

If the rotation of the groups in the molecular chain around the valence bonds is hindered by a high barrier potential, the internal motion of the chain is limited by the reaction of its different parts (for example, the polar groups) or by the great ramifying capacity of the chain; for a change of shape of the molecule under the influence of the external force, a long time interval is necessary. For this reason, such a macromolecule, when subjected to a fast-changing periodic force must have a rigid form. In lamina flow, with an increase of g, the deformation falls behind the phase of the acting force, and the amplitude of deformation increases more slowly than does g. The double refraction of a solution as a function of the rate gradient forms a curve deflected to the axis g. The $\Delta n = f(g)$ relation was experimentally derived for solutions of polymethyl methacrylate[2], whose molecules contain side polar groups, which govern the intramolecular reaction and the reinforcement of the chain.

In the present work, the characteristic discrepancy in the $\Delta n = f(g)$ curve was found for solutions both in hexane and in benzene.

Figure 4 gives the $\Delta n = f(g)$ relation for three fractions of sample A in benzene solution. Whereas for a lower-molecular fraction this relation is linear, the curve is deflected upward for high-molecular fractions. In Figure 5, the same relation is shown for solutions of sample A in hexane. Here a marked deflection of the curves toward the g axis is evident (for the first two fractions). In the light of this information, this means that the polybutadiene molecule is more inflexible in hexane solution than in benzene.

Evidently this increase of rigidity is conditioned by the weakness of the reaction with the solvent, with a corresponding increase of the role of the intermolecular reaction, and, consequently, is accompanied by a notable convolution of the chain.

It is characteristic that this decrease of flexibility in a poor solvent is more clearly observed in relatively high-molecular fractions and in polymers prepared at lower temperatures.

DYNAMIC-OPTICAL PROPERTIES AND MOLECULAR WEIGHT OF POLYMERS

As was previously shown, the values of the dynamic-optical constants X obtained for various samples are given in Tables 1, 2, and 3. For an explanation of their relation to the molecular weight, it is best to add log X to the graph

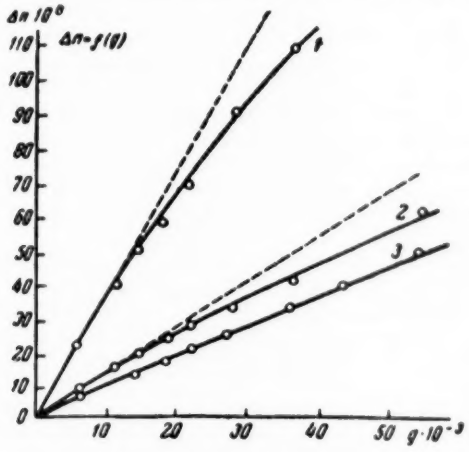

FIG. 5.—Uncompounded polybutadiene, prepared by polymerization at 20° C, in hexane.

1. Fraction I $C_g = 1.74\%$; $\eta_r = 15.0$
2. Fraction II $C_g = 1.38\%$; $\eta_r = 8.5$
3. Fraction III $C_g = 1.83\%$; $\eta_r = 7.36$

as a function of the log of the molecular weight log X. Here the points which correspond to the particular sample (A, B, and C) lie nearly on a straight line. Consequently, the relation sought can be expressed thus:

$$X = C \cdot \mu^a \tag{3}$$

where C and a are constants.

In this case, from the inclination of the corresponding curves for samples A and B, the factor $a \approx 0.9$, and for sample C, $a \approx 0.65$.

Thus, just as for loaded polymers[2], the dynamic-optical constants of the various fractions of samples A and B are roughly proportional to their molecular weights, so also for sample C, with an increase of μ, X increases more slowly.

Measurement of the angle of orientation of double refraction α permits the calculation of the coefficient of rotary friction of a molecule, W, according to the well known equation[11]:

$$\tan 2\alpha - \tan 2\alpha_0 = \frac{6kT}{g\eta W} \tag{4}$$

The coefficient W, calculated according to Equation 4 for benzene solutions, is recorded in the last column of Tables 1, 2, and 3.

We see that the values of W increase with increase of the molecular weight. If a logarithmic scale is used, the relation of W to μ can be determined very precisely by means of an equation similar to Equation 3. Then the value of a (in this case) is of the order of $a \approx 1.4$ for samples A and B; this corresponds to the results obtained earlier with loaded polymers[2]. Because of their unreliability, values of W for sample C are not given.

As contemporary theory shows[3], for an ideal model, *i.e.*, a solution of linear statically convoluted chain molecules with no side chains, all the particles of which are wetted by the solvent, the dynamic-optical constant X increases proportionally to the molecular weight μ, as W increases in proportion to μ^2. However, in the absence of free flow of solvent through the globule, *i.e.*, where there is a screening effect or only partially flowing globules, the coefficient of friction of a molecule of the same geometric dimensions will be less than, and proportional to, this. X will increase with an increase of μ slower than μ increases, and W will increase more slowly than μ^2. Evidently the increased compactness of the molecular structure, caused, for example, by side-chain formation to a large degree, can be explained in the same way. It is natural to expect that the degree of ramification and the opacity of the globule are properties which influence each other, since the increase of compactness of the globule, *i.e.*, the increase of the degree of ramification of the molecule, must also cause a greater screening effect in the solvent.

Thus the relation that we obtained between the values of X and W and the molecular weight indicates that the macromolecules of polybutadiene behave in solution as partially flowing globules. There is no doubt that the decrease of transparency of the globule is attributable to the compactness of the structure of the polybutadiene molecule, resulting from the extensive development of the side chains.

For this reason, the fact that sample C shows a smaller a value in Equation 3 by comparison with the two previous samples, must be considered a proof of the greater compactness of its molecular structure.

EFFECT OF TEMPERATURE OF POLYMERIZATION

In the investigation of the effect of the solvent on the dynamic-optical properties of solutions, we have seen that the increased rigidity of the polymer chain in a poor solvent is clearly observed in a polymer prepared at relatively low temperature (A). In solution in a good solvent, the molecular chain is rather flexible (see Figure 4).

Polymer C, obtained at 60° C, behaves differently. Figure 6 shows the $\Delta n = f(g)$ relation for two fractions of this sample dissolved in benzene and

hexane. The graphs for both solvents show a declivity to the g axis. Thus the chain molecules of the C polymer appear more inflexible than in polymers A and B. The data in the preceding paragraph showed that they also possess a very compact structure.

Under the same influence of the solvent, the more compact or looser structure of the macromolecules of the polymer may depend on different factors. If the monomer molecule contains in all one double bond and, consequently, the polymeric chain can not possess side chains, then its compact structure is determined entirely by the degree of its convolution, that is, by the forces reacting between the particles, in other words, by the height of the barrier potential corresponding to the rotation of the groups around the valence bonds.

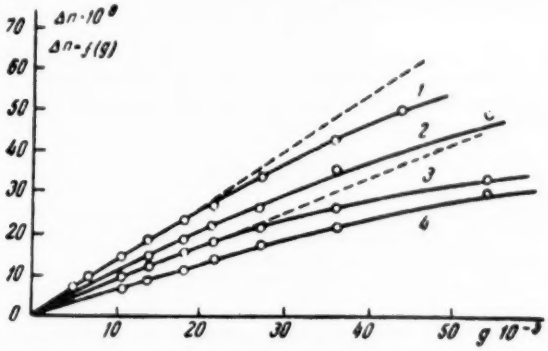

FIG. 6.—Uncompounded polybutadiene, prepared by polymerization at 60° C.

1. Fraction I in benzene: $C_s = 1.16\%$; $\eta_r = 6.86$
2. Fraction I in hexane: $C_s = 1.07\%$; $\eta_r = 4.6$
3. Fraction III in benzene: $C_s = 3.54\%$; $\eta_r = 7.25$
4. Fraction III in hexane: $C_s = 3.0\%$; $\eta_r = 4.5$

In this case the more rigid chain will be more extended, that is, it will have a looser structure. On the other hand, if the polymeric chain contains side chains, *i.e.*, two or more double bonds in the molecule of the monomer, then the compact structure of the macromolecule will depend on the degree of side-chain formation on the main chain. Thus a more highly developed chain has a more compact and more rigid structure.

The molecules of polymer C are distinguished from the other two samples by a greater compactness and greater solidity. In connection with what has been said above, this means that they are constructed of more highly ramified chains.

Thus, the study of the dynamic-optical properties of a polymer in solution shows that an increase of the temperature of polymerization leads, not only to a decrease of the mean molecular weight of the specimen, but also to a more highly complex molecule.

The value qualitatively characterized as solidity of the molecular chain is reflected in the time of relaxation of anisotropy τ which appears in the macromolecule during ramification. Since the deflection of the $\Delta n = f(g)$ curve (see Figure 6) is related to the relaxation of anisotropy of the chain in the periodic field of force, the order of τ can be estimated by means of the equation:

$$\frac{\Delta n}{\Delta n_0} = \frac{1}{\sqrt{1 + \omega^2\tau^2}} \tag{5}$$

where Δn is the observed double refraction of the solution, Δn_0 is the double refraction of the solution of globules ramified with practically no loss of time, and ω is the cyclic frequency of the periodic stretching force. For a particle whose shape is nearly spherical and which is in laminar flow with the rate gradient g, ω is equal to the angular speed of rotation, and thus: $\omega \approx g/2$.

As shown by experiment, in the case of flexible filiform molecules with the same degree of polymerization as that of the substances depicted in Figure 6, the $\Delta n_0 = f(g)$ relation is practically linear. The $\Delta n_0 = f(g)$ curves are constructed in Figure 6 as tangents to the corresponding $\Delta n_0 = f(g)$ curves at the point $g = 0$. Using these, for example for the $\Delta n_0 = f(g)$ curve at $g = 50.10$, we find:

$$\frac{\Delta n_0}{\Delta n} = \frac{43}{34} = 1.28$$

Introduction of these values into Equation 5 gives the value $\tau \approx 3 \times 10^{-5}$. This value corresponds well with the experimental results of studies of acoustic double refraction in solutions of polymeric substances[12].

CONCLUSIONS

Data obtained by a study of the dynamic-optical double refraction of solutions of various fractions of polybutadienes which had been prepared at various polymerization temperatures are presented.

The relation between double refraction and the rate gradient generally has the form of a curve. However, the halos and the sign of the curvature vary for the same sample in different solvents, as well as for samples polymerized at different temperatures in the same solvent, and the time of deformation relaxation of the macromolecules of polymer in solution is measured by the curvature of these curves.

On the basis of these data, conclusions are drawn regarding the shape of the macromolecules in various solvents and the influence of the temperature of polymerization on the configuration of the molecules.

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STUDIES OF THE MECHANISM OF MASTICATION OF RUBBER

V. THE VISCOSITY LOWERING OF RUBBER SOLUTIONS BY PHENYL DISULFIDE DERIVATIVES *

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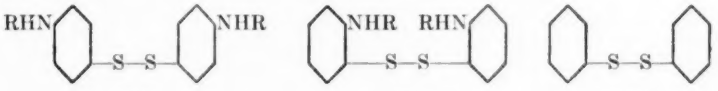
In our previous work[1], the viscosity lowering of rubber solutions by means of some compounds which give free radicals by decomposition was observed. Also the action of the amines on the viscosity lowering by radicals was investigated. In the present work we synthesized nine derivatives of phenyl disulfide, and the viscosity lowering of toluene solutions of natural and deproteinized rubber by some of them was investigated.



(I) (II) (III)

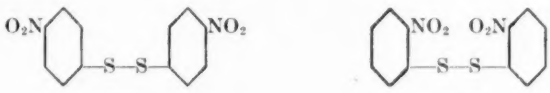
Recently it has been confirmed that phenyl disulfide (III) gives rise to free radicals by thermal decomposition of the S—S bond[2], that the radicals generated are able to dehydrogenate coexisting substances[3], and that the dissociation energy of the S—S bond is 53.9 kcal.[4].

EXPERIMENTAL

SYNTHESES OF PHENYL DISULFIDE DERIVATIVES

0.5 Mole of *o*- or *p*-chloronitrobenzene was boiled for 8–9 hours with 1.3 moles of sodium sulfide and 2 liters of water, and, after cooling, chloroaniline as a byproduct was removed by steam distillation. The remaining solution was slightly acidified with hydrochloric acid and oxidized with 5 cc. of 30 per cent hydrogen peroxide. The yellow crystals were filtered and recrystallized from alcohol. *o*- or *p*-Bis(aminophenyl) disulfide (A or B) was obtained. This was converted to C, D, E, F, and G by *N*-acetylation, *N*-benzoylation and *N*-*p*-nitrobenzoylation (see Table 1).

Independently the reaction product of chloronitrobenzene with sodium sulfide in alcoholic solution was recrystallized from benzene toluene. IV and V were obtained.



(IV) (V)

* Reprinted from the *Journal of the Institute of Polytechnics*, Osaka City University, Vol. 2, No. 2, pages 209–216, July 1952.

TABLE I

MELTING POINTS AND ANALYSES OF PHENYL DISULFIDE DERIVATIVES

Compound	Structure (R group in compound I or II)	Melting point (° C)	Sulfur content (%) Observed	Calculated
A	H in II	88–90°	25.82	25.81 as $C_{12}H_{12}N_2S_2$
B	H in I	76–77°	25.69	
C	CH_3CO in II	153–155°	19.00	19.27 as $C_{16}H_{16}O_2N_2S_2$
D	CH_3CO in I	184.5–186°	19.30	
E	C_6H_5CO in II	140–142°	13.85	14.01 as $C_{26}H_{20}O_2N_2S_2$
F	C_6H_5CO in I	>250°	14.01	
G	p-$O_2NC_6H_4CO$ in I	209–212° (decompn.)	11.74	11.72 as $C_{26}H_{18}O_6N_2S_2$
H	V	191–193°	20.70	20.78 as $C_{12}H_8O_4N_2S_2$
J	IV	180–182°	20.34	

In addition, recently, bis-(*o*-benzoylamino-phenyl) disulfide (E)* has been reported to have been used as an accelerator of mastication (peptizer) at elevated temperatures.

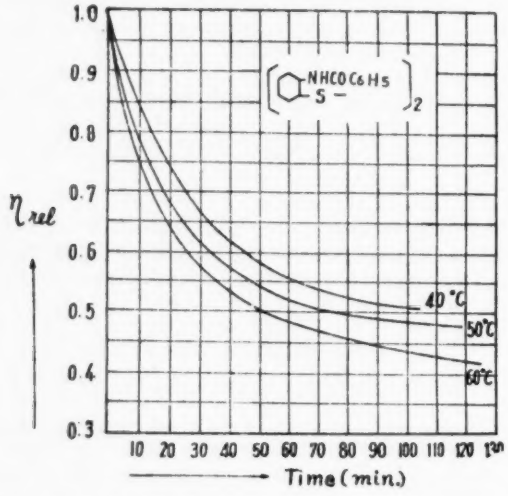


FIG. 1.—Viscosity lowering of a solution of natural rubber by compound E.

VISCOSITY LOWERING OF RUBBER SOLUTIONS

Method.—In the case of natural rubber, the experimental method was the same as that of the previous report. 1.5 cc. of 0.85 per cent toluene solution of smoked sheet rubber, 2 cc. of toluene solution containing 4.75×10^{-5} mole of phenyl disulfide derivative, and 1.5 cc. of toluene were pipetted into an Ostwald viscometer. The mixture in the viscometer then contained 0.255 per cent of rubber, and the concentration of the disulfide was 0.25 mole per mole of rubber as C_5.

In the case of deproteinized rubber, the same procedure was used, except that 1.5 cc. of 0.75 per cent toluene solution of deproteinized rubber was used. This mixture corresponded to the 0.237 per cent rubber solution. The disulfide content was 0.38 mole per C_5 of rubber.

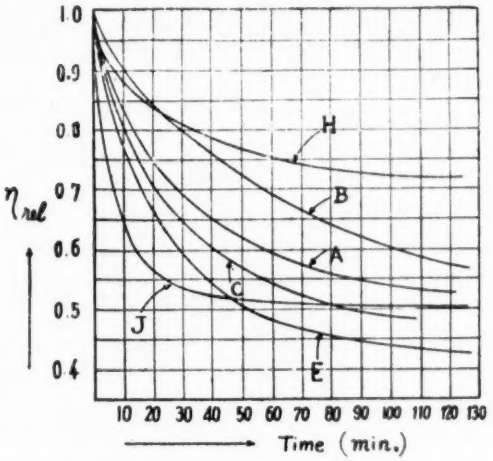


FIG. 2.—Viscosity lowering of a solution of natural rubber by compounds A, B, C, E, H, and J at 60° C.

The Ostwald viscometer was placed in a thermostat regulated at 40, 50 or 60 ± 0.2° C, and the changes of relative viscosity, η_{rel} (based on the initial η_{rel} values of 1), were observed by measuring the dropping time at definite intervals.

Results.—The viscosity changes, for example, in the case of E, bis-(*o*-benzoylaminophenyl) disulfide, for natural rubber, are shown in Figure 1. The same observations were made with both natural and deproteinized rubber, using A, B, C, E, H, and J, respectively (D, F, and G were not used since they were insoluble). All had shown similar trends of viscosity lowering, although the magnitude of the lowering differed. Accordingly, it is useless to report here all the values. Instead, comparisons between the mixtures at 60° C are shown in Figures 2 and 3.

From these figures, the following results were obtained.

(1) The magnitudes of the viscosity lowering are larger for natural rubber than for deproteinized rubber.

(2) In the case of R=H, the *o*-system has a greater effect than that of the

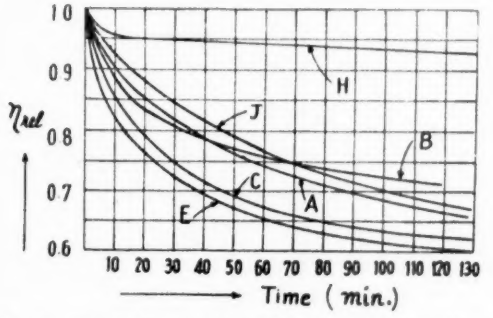


FIG. 3.—Viscosity lowering of a solution of deproteinized rubber by compounds A, B, C, E, H, and J at 60° C.

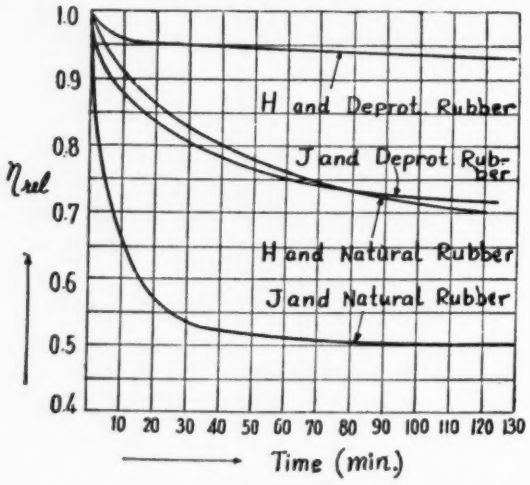


FIG. 4.—Decrease of the η_{rel} by dinitrophenyl disulfides at 60° C.

p-system toward natural rubber, but no remarkable difference toward deproteinized rubber.

(3) In the case of the *o*-system (II), substituents attached to the phenyl group act effectively in the order: $C_6H_5CONH > CH_3CONH > NH_2$. However, in the case of the *o*- or *p*-nitrosubstituted systems of IV and V, the *p*-substances are far more effective than *p*-substances, as shown in Figure 4, although the magnitude of the viscosity lowering is greater for natural rubber, as in the previous cases.

Furthermore, the velocities of the viscosity lowering ($d\eta_{rel}/dt$) for each case,

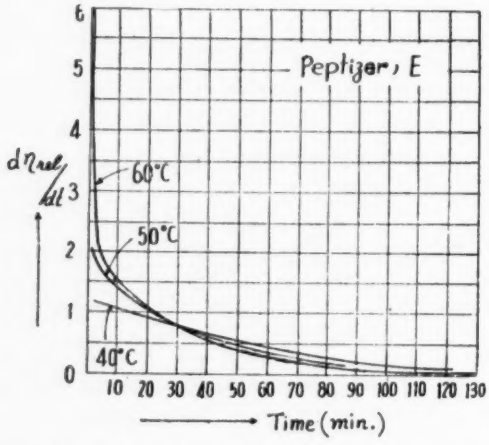


FIG. 5.—Changes of the rate of η_{rel} lowering of a solution of natural rubber with time.

were calculated. For instance, in the representative E case, the results were obtained as Figures 5 and 6. In every case, the same tendency for the velocity to decrease rapidly at first and approach zero asymptotically was observed.

Moreover, if the reciprocals of time z, in which η_{rel} came to a definite value, are proportional to the reaction velocity, the activation energy could be calculated by the following equation:

$$\frac{1}{z} = k.e^{-E/(RT)}$$

Figure 7 shows this relation for natural rubber with the peptizer E. Table 2 shows the calculated results for each case.

In Table 2, it is evident that the activation energies are very small, and also that, in general, natural rubber gives the lower values. As for the values of *o*-derivatives, they agree with the observations of η_{rel} in Figures 2 and 3, *i.e.*,

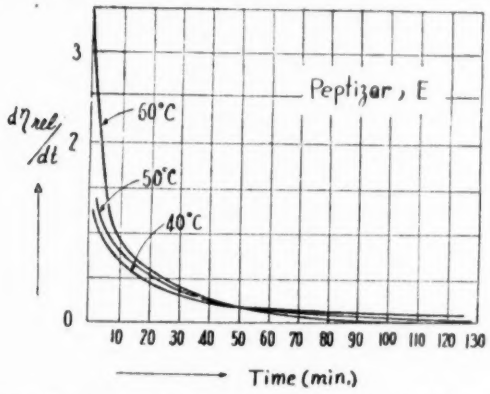


FIG. 6.—Changes of the rate of η_{rel} lowering of a solution of deproteinized rubber with time.

TABLE 2

ACTIVATION ENERGY OF VISCOSITY LOWERING (CALORIES)

	Accelerator for mastication	Natural rubber	Deproteinized rubber
A	(*o*-NH_2)	7000	13,000
B	(*p*-NH_2)	9400	12,600
C	(*o*-CH_3CONH)	6300	11,000
D	(*o*-C_6H_5CONH)	5800	9,400

the values decrease in the order: $NH_2 > CH_2CONH > C_6H_5CONH$. The *p*-substituted compound had the larger value.

DISCUSSION OF RESULTS

We have considered that the viscosity lowering of rubber solutions is mainly due to fission of the chains of rubber hydrocarbon molecules by free radicals. The important problem is, therefore, whether the disulfides used here are able to decompose hydrocarbon molecules radically. There are no direct factors to determine the ease of dissociation of S—S bonds, but Walsh[5] has pointed out

the following four factors: electronegative effects of the bonded groups, polarization of bond, repulsion of filled atomic orbitals, and overlap of atomic orbitals.

Here we shall consider only the system of *o*-substituted derivatives. When substitution is effected with the NH_2 radical alone, the electromeric effect is as in the above formulas, but the effect becomes smaller as R changes: H >

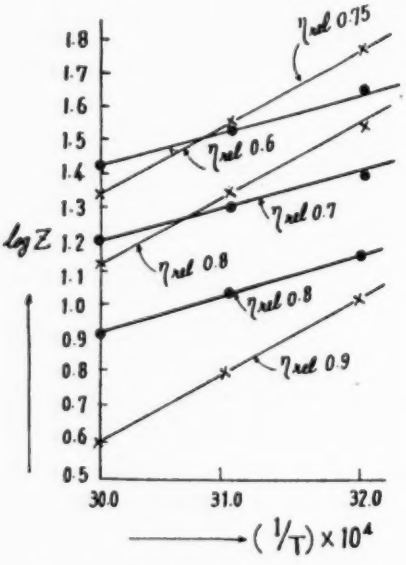


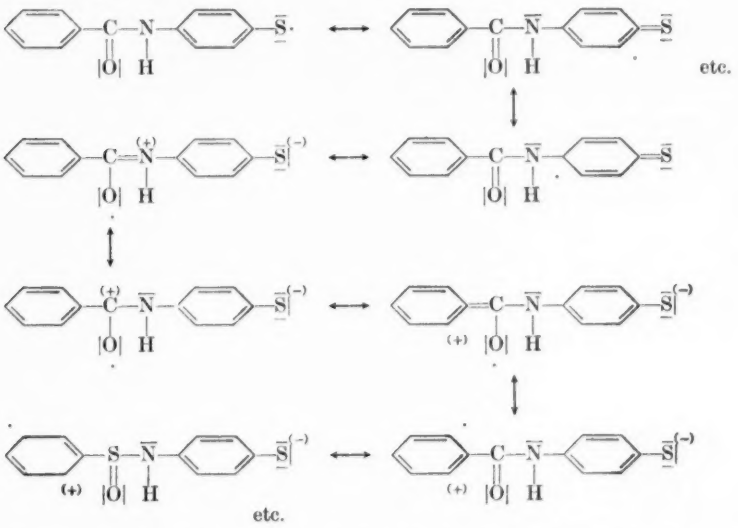
FIG. 7.—Data obtained with compound E.

$COCH_3$ > COC_6H_5. In other words, the electron density around S reaches its maximum with NH_2; accordingly, the linkage between S—S should become stronger.

In the case of the derivatives of benzoyl peroxide, the relations are the opposite, because the oxygen atom can not expand its valency shell above 8. Hence, some electron-releasing substitute, such as CH_3O or NH_2, is introduced into the *p*- or *o*-position, and the decomposition tendency of benzoyl peroxide increases, as indicated by Swain, Stockmayer, and Clarke[6].

This agrees with the above experimental results. However, steric hindrance and strain by *o*-orientation must also have serious effects on the dissociation of the bond. It has often been recognized that, in the formation of the triphenylmethyl radical, *o*-substituted compounds decompose much more vigorously than do *p*-substituted compounds, and this is related to the *o*-effect in general. Also in the case of benzoylamino radicals, we can assume that the dissociation is facilitated by the occurrence of the so-called F-strain.

Moreover, there is a noticeable influence of resonance. On the expectation that the coplanar configuration is more favorable to the free radical formed than the compound before decomposition, in the case of *o*-substitution at least, it may be assumed that the resonance energy of the free radical formed becomes larger. When CH_3CONH- or C_6H_5CONH- is introduced into the benzene nucleus, it can make the corresponding resonance hybrid, and the resonance energy of the radical may have the largest value with C_6H_5CO-, as shown by the following scheme:



It appears that these various effects add up to produce the above results; at any rate, almost all the experimental results can be explained theoretically, with the exceptions of the bis(nitrophenyl) disulfides, which belong to another system. These cases will be considered at the next opportunity.

SUMMARY

Nine derivatives of phenyl disulfide having substituents in the *o*- or *p*-position, were synthesized, and the lowering of the viscosity of toluene solutions of rubber by means of these derivatives was measured. Compounds substituted in *o*-position were more effective than were compounds substituted in *p*-position, and the effects of the substituents were in the order: $C_6H_5CONH > CH_3CONH > NH_2$. These conclusions are in agreement with electronic interpretations.

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THE ROLE OF CARBON BLACK IN THE ACTION OF LIGHT ON RUBBER *

Y. S. Zuyev

The action of light on rubber was studied with reference to the rate of elongation at constant stress of films, 100–150μ thick, obtained from solutions of rubber to which channel carbon black had been added by milling. The measurements were made in an apparatus, described earlier[1], which was equipped with a rolling carriage. When structure formation takes place as a result of irradiation of a film, the film stretches more slowly than one that has not been irradiated. If the structure is destroyed, the film elongates at a faster rate.

The films were irradiated by a mercury quartz lamp P RK-2 in air at a distance of 5 cm., both when relaxed (preliminary irradiation) and while stretched (continuous irradiation). The light filters listed in Table 1 were used.

TABLE 1

Light Filter	Penetration in Å units
Pyrex glass	2967 and more
Black ultraviolet glass	2967–4046
Colloidal dispersion of carbon black	3341–4358
Ferrichloride (0.1 *N* solution)	4046 and more
Copper sulfate + nickel sulfate	2537–4358

The average temperature in the experiments was 25° ± 0.1° C. A film was stretched in the quartz apparatus, which was equipped with a jacket, about 1 cm. thick, in which distilled water or a solution of the light-filtering substance was circulated. The water and also the solutions were provided with an ultrathermostat. The temperature of the water leaving the jacket was measured by a thermometer, and was kept constant within ± 0.1° C.

The temperature of the film itself during irradiation, measured by a thermocouple in supplementary experiments, proved to be higher than the temperature of the thermostatically controlled liquids. When the constant mean temperature of a pure-gum rubber-film during irradiation was 25° C, the temperature of the thermostatically controlled liquid remained constant at 24° C; when the films contained carbon black or Sudan black, the temperature remained at 23.5° C.

We know that when light acts on a film of divinylstyrene or polychloroprene rubber not under stress, carbon black acts as a good protective agent. A similar action of carbon black had also been shown previously for polybutadiene (see Figure 1) and Butyl rubbers.

When films of these rubbers are irradiated under stress in the presence of carbon black, the rate of deformation increases sharply. For example, Figure 1 gives the data for polybutadiene rubber (E is the relative deformation in per

* Translated for Rubber Chemistry and Technology by Alan Davis from the *Doklady Akademii Nauk SSSR* (*Reports of the Academy of Sciences USSR*), Vol. 82, No. 6, pages 935–938 (1952).

cent). For polyisobutylene, deformed under identical conditions but without irradiation, as well as with continuous irradiation through Pyrex glass (under the given conditions, light has no perceptible effect on it), the rate of deformation also sharply increases when carbon black is added (see Figure 2).

In explaining the cause of this phenomenon, it was necessary to establish: (1) the specific effect of carbon black, that is, whether there are any other substances having a similar action, (2) the relation of the effect to the concentration of carbon black in rubber, (3) which part of the light acts on rubber containing carbon black, and (4) the nature of the process caused by light in this case.

Further experiments showed the following facts.

(1) Black Sudan dye in Butyl rubber (1 per cent) and in polybutadiene (2 per cent) acts even more effectively than does carbon black (Figure 1, curves 11, 12).

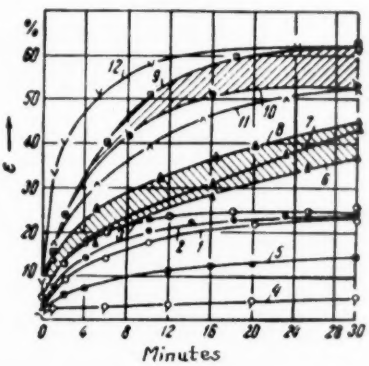

FIG. 1.—Kinetics of deformation of polybutadiene at uniform stress under different conditions of irradiation. Pure rubber: 1. without light, 2. continuous irradiation with light filter, 3. continuous irradiation without light filter, 4. preliminary irradiation 10 minutes without light filter.

Rubber and carbon black: 5. preliminary irradiation 10 minutes without light filter, 6. continuous irradiation with light filter (1% carbon black), 7. continuous irradiation with light filter (5 and 25% carbon black), 8. continuous irradiation with light filter (0.2% carbon black), 9. continuous irradiation without light filter (25% carbon black), 10. continuous irradiation without light filter (5% carbon black) (SKB and Sudan black 2%), 11. continuous irradiation with light filter, 12. continuous irradiation without light filter.

(2) There is no definite concentration relation in the action of carbon black (the concentration was increased from 0.2 to 25 per cent in the mixture (Figure 1, curves 6–10)). The behavior of carbon black in such small concentrations as 0.2 per cent indicates that its action is not connected with its action as a filler and displacement of the chains, but is purely optical. This is confirmed by the similar behavior of Sudan black, which has almost the same absorption spectrum in ultraviolet light as does carbon black.

(3) Continuous irradiation of polybutadiene through a colloidal solution of carbon black, as well as through black glass, slows down the deformation of a rubber film (see Figure 3); that is, the ultraviolet light admitted by these filters causes some structure formation in the film; and apparently the cause of the increased rate of deformation of a rubber film in the presence of carbon black is the light absorbed by the carbon black.

For additional proof of this, the action of visible light (light filter a 0.1 *N* ferric chloride solution) absorbed by carbon black was tested with films of polybutadiene and polyisobutylene. In the presence of carbon black we again observed a large increase of rate of deformation during continuous irradiation.

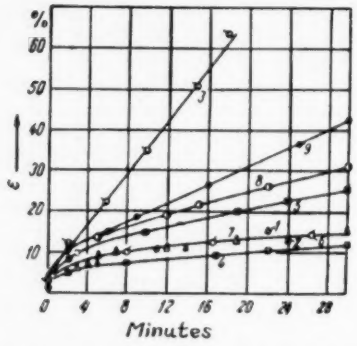

FIG. 2.—Kinetics of deformation of polyisobutylene. 3% carbon black: 1. without irradiation, 2. preliminary irradiation 30 minutes, 3. continuous irradiation. 0.5 per cent carbon black: 4. without irradiation, 5. continuous irradiation through 0.1 *N* solution of ferric chloride. Without carbon black: 6. without irradiation, 7. continuous irradiation, 8. without irradiation, temperature 70° C, 9. continuous irradiation, temperature 70° C.

while light had no effect on films without carbon black under these same conditions (see Figure 3).

After preliminary irradiation of carbon-treated films of polybutadiene and polyisobutylene, there were no noticeable changes of mechanical properties (see Figure 2, curve 2; Figure 3, curve 6). This indicates the absence of any chemical process in this case.

The constancy of viscosity of polyisobutylene solutions prepared from films containing carbon black (Figure 2, curves 1–5; Table 2) also indicates the absence of a destructive process in the films, despite the increase of rate of deformation under the influence of light. Viscosity is a very sensitive index

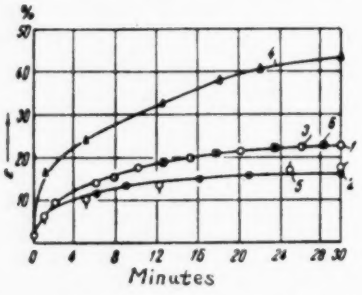

FIG. 3.—Kinetics of deformation of polybutadiene. 1. without irradiation, 2. continuous irradiation through cobalt sulfate + nickel sulfate, 3. continuous irradiation through 0.1 *N* ferric chloride + Pyrex glass. Polybutadiene with carbon black. 4. continuous irradiation through 0.1 *N* ferric chloride + Pyrex glass, 5. continuous irradiation through a colloidal solution of carbon black, 6. preliminary irradiation.

of structural changes in high polymers. A small difference in the rate of deformation of films with 0.5 and 3 per cent carbon black (see Figure 2, and Table 2) also indicates the absence of a destructive process in the films, despite the increase of rate of deformation under the influence of light. Consequently the increase of rate of deformation during continuous deformation of rubbers containing carbon black can not be explained as an increase or commencement of destructive processes which are characterized by a decrease of molecular

weight. It seems to us that the only possible explanation of this phenomenon is the increased activity of the individual segments of the rubber chains at the points where they come in contact with the particles of carbon black.

The light energy absorbed by the carbon black under these experimental conditions would be quite sufficient to heat the carbon black particles several hundred degrees per minute, in the absence of any heat loss. A large heat loss prevents the heating of the entire film and the radiation then absorbed does not

TABLE 2

Carbon black content (per cent)	Conditions of irradiation	Relative viscosity of 0.2 per cent solution
3	Without irradiation	1.4
3	Preliminary irradiation for 30 minutes	1.4
3	Continuous, through Pyrex glass	1.4
0.5	Without irradiation	1.7
0.5	Continuous irradiation, through 0.1 *N* ferric chloride	1.7

change the temperature. Local momentary heat loss takes place in the segments adjoining the carbon black particles; this, without causing destruction of the chains, greatly increases their reactivity.

The rate of deformation during continuous irradiation of polyisobutylene containing carbon black is greater than the rate under the same conditions for films at 70° C (curve 3 of Figure 2 is much higher than curve 8, which represents 70° C). At a temperature of 70° C throughout the film and simultaneous irradiation, destruction of polyisobutylene is observed (Figure 2, curves 8 and 9), and the viscosity of the corresponding solutions falls from 1.8 to 1.7.

The widely held notion about the low light resistance of polyisobutylene is evidently to be explained by the fact that changes were usually observed under the influence of direct solar radiation, that is, a condition whereby the temperature is raised considerably. At ordinary temperatures, *e.g.*, 25° C, polyisobutylene, as seen from our data, resists the influence of light in which the short ultraviolet band is absent.

ACKNOWLEDGMENT

We wish to acknowledge the assistance of T. A. Kokyena in carrying out the experiments.

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SORPTION OF GR–S TYPE OF POLYMER ON CARBON BLACK. III. SORPTION BY COMMERCIAL BLACKS *

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The sorption of GR-S type of polymers in solution on Graphon carbon black under different experimental conditions has been described in two previous papers[1]. Graphon, with its partially graphitized surface, is not a commercial type of black. For this reason, four commercial carbon blacks have been employed in an extension of previous studies. Following a comparison of the sorption capacities of the four blacks, the effects of solvent, degree of unsaturation, molecular weight, and previous heat treatment of the carbon black are considered. Some experiments with rubber fractions of high and low molecular weight and with carbon columns are reported. The sorption of two low-temperature rubbers is compared with the standard GR-S prepared at 50° C. Finally, some results of a preliminary study of "bound" rubber, that portion of the rubber which is insolubilized in benzene by intimate mixing with carbon black, are given.

Materials.—Reagent grade benzene, chloroform and carbon tetrachloride, absolute ethanol, *n*-heptane (research grade, 99 mole-per cent purity, from Phillips Petroleum Co.), and technical grade xylene and toluene were used as solvents.

The carbon blacks used and some of their properties supplied by the manufacturers are listed in Table I.

TABLE I

SOME PROPERTIES OF THE CARBON BLACKS EMPLOYED

Carbon black	Type	Nitrogen surface area (sq. m./gram)	Electron microscope area (sq. m./gram)	Producer
Vulcan-1	Reinforcing furnace	109	98	Godfrey L. Cabot, Inc.
Graphon	[a]	85		Godfrey L. Cabot, Inc.
Sterling-105	Fine furnace	99	75	Godfrey L. Cabot, Inc.
Philblack-A	High modulus furnace	39	52	Phillips Petroleum Co.
Philblack-O	High abrasion furnace	82	84	Phillips Petroleum Co.

[a] Graphon is prepared by induction heating of Spheron-6, a medium processing channel black, to 3200° over a period of two hours. The nitrogen area of Spheron-6 is given as 106 sq. m./gram, the electron microscope area as 120 sq. m./gram[2].

GR-S type rubber of different degrees of unsaturation, conversion approximately 60 per cent, was prepared by the mutual recipe at 50° C, a varying ratio of monomers being used in the charge. GR-S X-418 was obtained from

* Reprinted from the *Journal of Physical Chemistry*, Vol. 56, No. 6, pages 740–745, June 1952. This work was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Synthetic Rubber Program of the United States Government. The present address of R. G. Gutmacher is the J. T. Baker Chemical Co., Phillipsburg, New Jersey.

the Government Pilot Plant, Akron, Ohio. Two samples of cold rubber, polymerized at +5 and −10°, respectively, were obtained through the courtesy of C. F. Fryling, Phillips Petroleum Company.

Procedure.—In general, 0.25 per cent solutions of polymer in the various solvents were prepared. One hundred cc. of solution was shaken with a certain weight of carbon black at 30°, usually for a period of 40 hours. After centrifuging, 25-cc. aliquots of the supernatant liquid were evaporated to determine the amount of residual rubber.

In some experiments with chloroform solutions and other solvents, especially benzene, it was necessary to apply a correction for the amount of carbon

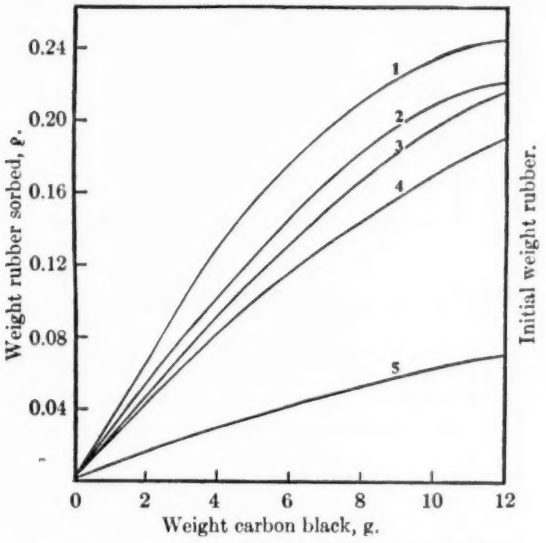

FIG. 1.—Sorption of GR-S from chloroform solution by various carbon blacks: (1) Spheron-6; (2) Vulcan-1; (3) Philblack-0; (4) Sterling-105; (5) Philblack-A.

black colloidally suspended in the solution, and weighed with the unsorbed rubber. Details of the procedure for the determination of black in rubber are contained in another publication[2].

EXPERIMENTAL RESULTS

Comparison of the Sorption Capacities of the Carbon Blacks.—The sorption of GR-S from chloroform and *n*-heptane solution by the various carbon blacks was determined, following the general procedure given above. The sorption isotherms are plotted in Figures 1 and 2. In both solvents, the arrangement of the carbon blacks in order of decreasing sorption is the same: Spheron-6 (Graphon), Vulcan-1, Philblack-O, Sterling-105, Philblack-A. The low solvent power for rubber of *n*-heptane, which was previously noted in sorption studies with Graphon, decreases the relative differences in sorption characteristics of the carbon blacks. The sorption is found not to be directly related to surface area.

Sorption of Rubber from Various Solvents.—A sample of GR-S of 57.5 per

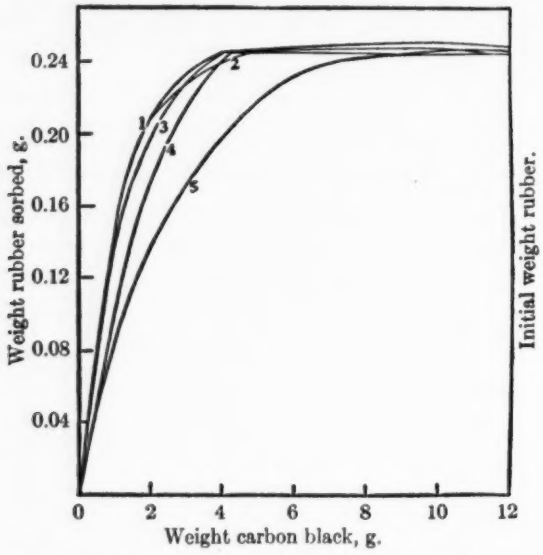

FIG. 2.—Sorption of GR-S from *n*-heptane solution by various carbon blacks: (1) Spheron-6; (2) Vulcan-1; (3) Philblack-0; (4) Sterling-105; (5) Philblack-A.

cent conversion was used to prepare 0.25 per cent solutions in benzene, chloroform, *n*-hexane, chloroform-*n*-hexane (1:1 by volume), and benzene and chloroform with varying amounts of ethanol added. The sorption on varying

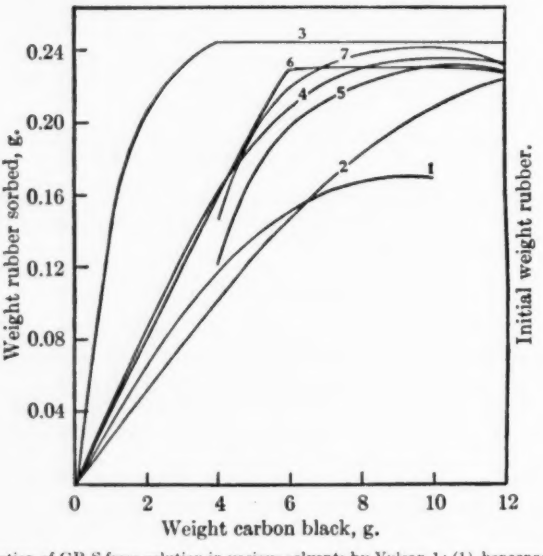

FIG. 3.—Sorption of GR-S from solution in various solvents by Vulcan-1: (1) benzene; (2) chloroform; (3) *n*-heptane; (4) chloroform-*n*-heptane (1:1); (5) chloroform-ethanol (9:1); (6) chloroform-ethanol (8:2); (7) benzene-ethanol (9:1).

amounts of Vulcan-1 was determined by the usual procedure. The results are plotted in Figure 3. In Figure 4 the weight of rubber sorbed per gram of Vulcan-1 is plotted against the final equilibrium concentration in solution. The curves represent sorption isotherms at room temperature. The greatest amount of sorption is obtained from *n*-heptane solution, and thereafter, in decreasing order, from chloroform-*n*-heptane (1:1), chloroform-ethanol (8:2), benzene-ethanol (9:1), chloroform-ethanol (9:1), benzene and chloroform.

The addition of ethanol to benzene or chloroform, which decreases the solvent power toward rubber, gives an expected increase of the sorption.

Sorption of Low-Temperature Rubbers.—The sorption of two samples of "cold rubber," polymerized at −10° and +5°, respectively, from 0.25 per cent

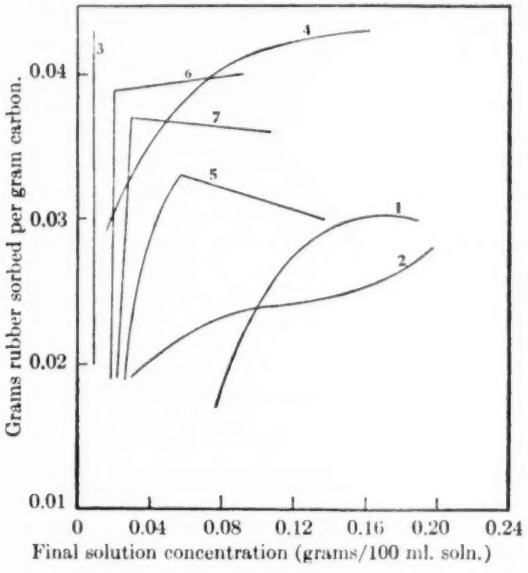

FIG. 4.—Variation of weight of rubber sorbed per gram of carbon black with final concentration for different solvents: (1) benzene; (2) chloroform; (3) *n*-heptane; (4) chloroform-*n*-heptane (1:1); (5) chloroform-ethanol (9:1); (6) chloroform-ethanol (8:2); (7) benzene-ethanol (9:1).

solution in chloroform and 90% benzene −10% ethanol (by volume) by Vulcan-1 was studied. The two rubber samples were polymerized by the Phillips Petroleum Company "Custom recipe," and were stated to be gel-free. The sorption data, obtained after 40 hours' shaking various amounts of Vulcan-1 with 100-cc. portions of the rubber solutions are plotted in Figure 5.

The sorption curves exhibit no striking differences. Twelve grams of Vulcan-1 sorb 84 per cent of the −10° rubber, 75 per cent of the +5° rubber, and about 86 per cent of 50° GR-S from chloroform solution. The somewhat lower sorption of the +5° rubber may be due to the fact that it contains about 9 per cent of rosin acid, rosin soap and antioxidant[4].

Effect of Previous Heat Treatment of the Carbon Black.—The manner of activation of carbon black determines the charge on its surface and the gases which remain adsorbed. Air-heating at 950° gives a positively charged surface, on which oxygen is adsorbed; air-heating at 450° leaves the surface

negatively charged[5]. If the carbon black is heated in an atmosphere of nitrogen at 500°, physically adsorbed oxygen is removed; heating at 1100° should remove combined oxygen also.

To determine the effect of heating carbon black on its sorption of rubber from solution, samples of Philblack-A, Vulcan-1 and Sterling-105 were heated at 500° and 1100° for eight hours in an atmosphere of nitrogen. After heating, they were allowed to cool under nitrogen and bottled.

Various amounts of the heated carbon blacks were shaken with 100 cc. of a

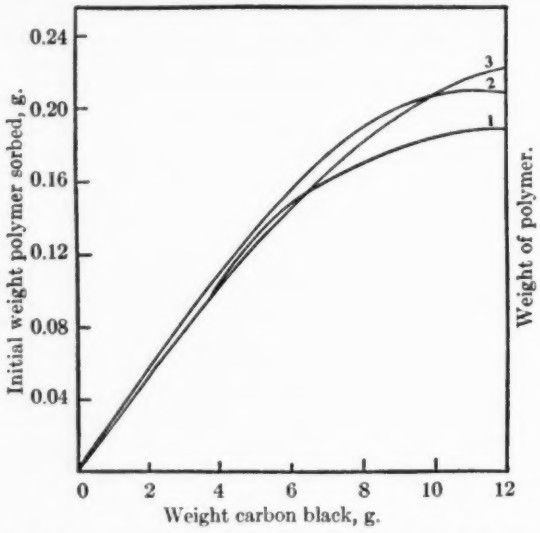

FIG. 5.—Sorption of low-temperature rubbers from chloroform solution by Vulcan-1: (1) R157 (polymerized at +5°); (2) R169 (polymerized at −10°); (3) GR-S (polymerized at 50°).

0.25 per cent solution of GR-S (66 per cent conversion) in benzene for 40 hours. The residual rubber in solution was determined.

By comparison with the sorption by the unheated carbon black of the same rubber solution, heating in nitrogen gave a 20 per cent increase in sorption by Philblack-A and Vulcan-1. A slight increase was also observed with Sterling-105. There was no significant difference between the sorption obtained on carbon black heated at 500 and 110° in nitrogen (Figure 6).

A sample of Vulcan-1 was heated in air in a loosely covered nickel crucible for periods of one, three and five hours at 425–450°. The weight loss was, respectively, 1.9, 5.3 and 7.1 per cent. The sorption of GR-S from benzene solution and from *n*-heptane solution was determined as before. It was found that the period of heating made almost no difference, and that the sorption by air-heated black from benzene solution was practically identical with that shown by unheated black. Air-heated carbon shows an increase in sorption from *n*-heptane solution; six grams of the heated carbon black give complete sorption of the GR-S, but with even 12 grams of the unheated Vulcan-1 about 3 per cent of the rubber remains in solution. Of course, the overall sorption from *n*-heptane is much greater than from benzene solution.

Sorption of Polymers of Various Degrees of Unsaturation and of Polystyrene.

TABLE II

SORPTION OF POLYMERS OF VARYING BUTADIENE–STYRENE RATIOS BY VULCAN-1

Wt. carbon black (g.)	75 Bu.–25 Styrene: Residual rubber (g./100 cc. soln.)	75 Bu.–25 Styrene: Rubber sorbed (g.)	50 Bu.–50 Styrene: Residual rubber, (g./100 cc. soln.)	50 Bu.–50 Styrene: Rubber sorbed (g.)
0	0.252	—	0.244	—
2	.198	0.054	.194	0.050
4	.148	.104	.149	.095
6	.108	.144	.110	.134
8	.075	.177	.078	.166
10	.052	.200	.058	.186
12	.036	.216		
	25 Bu.–75 Styrene		5 Bu.–95 Styrene	
0	0.252	—	0.263	—
2	.194	0.058	.214	0.049
4	.143	.109	.151	.112
6	.104	.148	.103	.160
8	.072	.180	.068	.195
10	.050	.202	.045	.218
12	.048	.204	.038	.225

—Polymers of varying butadiene-styrene ratios ranging from 75% butadiene-25% styrene to pure polystyrene were prepared by the mutual recipe at 50°. The conversion in each case was approximately 60 per cent. The sorption

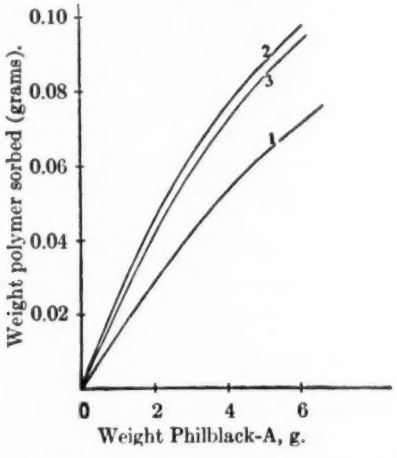

FIG. 6.—Sorption of GR-S on Philblack-A heated in nitrogen: (1) unheated; (2) heated at 500°; (3) heated at 1100°.

from 0.25 per cent solution in chloroform was determined with Vulcan-1 and Sterling-105. The data, as given in Table II, show that in the range 75% butadiene-25% styrene to 5% butadiene—95% styrene there is little change in the amount of polymer sorbed by a given weight of carbon black; the same was found with Graphon.

Pure polystyrene behaves in a different and striking manner. With Gra-

phon, a marked decrease in sorption of polystyrene was noted in comparison to the sorption of the copolymers with butadiene. Clear supernatant liquids could be obtained by centrifuging. When polystyrene was shaken with commercial carbon blacks, such as Vulcan, very dark supernatant liquids resulted and reliable sorption data could be obtained. However, it was found that when 10 or 12 grams of Vulcan-1 and polystyrene of high inherent viscosity (η = 12.2) in chloroform solution were shaken, a clear supernatant liquid resulted and the carbon was in large, spherical, rubbery balls at the bottom of the bottle. About 6 per cent of the polymer originally present remained in solution. Reagent grade chloroform, which contained about 0.7 per cent ethyl alcohol, was used as the solvent. Removal of the alcohol or the addition of more alcohol to bring the total concentration up to 2.7 per cent were found to make no difference. A more dilute solution of polystyrene in chloroform (0.065 g./100 cc. instead of the usual 0.25 g./100 cc. of solution) also gave no "bunching" effect with weights of Vulcan-1 less than 12 grams. It did not matter whether the carbon was added all at once or in portions at long intervals, as long as the final quantity was 12 grams of black in 100 cc. of polymer solution.

A time study of the sorption of polystyrene (η = 12.2) from 100 cc. of 0.25 per cent solution in chloroform on 12 grams of Vulcan-1 was made. The bunching effect was observed after 0.75 hour of shaking, but the liquid remained dark until after ten hours' shaking, after which time the supernatant liquid became perfectly clear. The time required for attainment of sorption equilibrium is fairly long in comparison with usual experience.

Experiments with high viscosity polystyrene (η = 9.8 and 3.8, respectively) and other carbon blacks showed that 10 or 12 grams of Philblack-A, 18–20 grams of Philblack-O or Sterling-105 are required to produce bunching. With low-viscosity polystyrene [η = 1.3, and 0.26 (made with thiol)] and Vulcan or other blacks, no bunching is found; the supernatant liquids are dark but transparent, and sorption data can be obtained. Philblack-A, which sorbs the smallest amounts of GR-S of any of the four furnace blacks, also sorbs the smallest amount of low-viscosity polystyrene. Up to 30 grams of Spheron-6, the only channel black tested, gave no bunching under any conditions.

Sorption of Rubber Containing Microgel.—In previous experiments, GR-S samples of about 60 per cent conversion were employed to avoid the complications caused by microgel, which is often present in polymer of 70 per cent conversion or higher. In studies with Graphon and benzene solutions of GR-S, it was found that microgel was not sorbed on Graphon, but that the sol fraction could be completely sorbed. The nature and behavior of microgel has been discussed in detail by Baker[6].

The sorption of two samples of GR-S of 74.7 and 81.5 per cent conversion in *n*-heptane solution on Vulcan-1 was investigated. The sorption isotherms of the whole rubbers were obtained in the usual manner. The gel content was determined by the method of Medalia and Kolthoff[7]. A portion of the rubber which had been milled and heated as required for gel determination was dissolved in *n*-heptane. The mixtures were filtered through glass wool, and the usual sorption experiments were performed with the filtrates. Both with the whole rubber and the sol fraction, the supernatant liquids were clear after centrifuging.

From the results of Table III it appears that microgel is sorbed as well as the sol fraction on Vulcan-1 from *n*-heptane solution. The small amount of unsorbed material may be the antioxidant, some fatty acid, or some very low molecular weight rubber.

Effect of Molecular Weight on Sorption.—A sample of X-418 rubber obtained from the Government Pilot Plant, Akron, was fractionated by the method of Carr, Kolthoff, and Carr[8]. Six fraction were obtained and their sorption from *n*-heptane solution was determined. The data are shown graphically in Figure 7. The intrinsic viscosities given[9] represent those of the

TABLE III

SORPTION OF MICROGEL-CONTAINING GR-S ON VULCAN-1 FROM *n*-HEPTANE

Vulcan (g.)	Residual rubber (g./100 cc. soln.) Conversion 81.5%	Rubber sorbed (%) Gel content 52%
	Whole rubber	
0	0.175	—
2	0.046	73
4	0.028	84
6	0.014	92
10	0.006	96
12	0.008	95
	Sol fraction	
0	0.216	—
2	0.041	81
4	0.010	95
6	0.005	97
10	0.006	97
12	0.004	98

polymer in benzene as the solvent; *n*-heptane gave values of 0.5 for all fractions.

Although there is some spread in the curve for the different fractions, on the whole the sorption does not vary appreciably from the fraction having a molecular weight of 433,000 ($[\eta] = 2.98$) to that of a molecular weight of 85,000 ($[\eta] = 1.00$). The sorption was appreciably greater with the molecular weight fraction of 596,000 ($[\eta] = 3.69$).

Effect of Time of Shaking.—The change in the amount of unsorbed rubber and the intrinsic viscosity of the solution with time of shaking has been considered previously. Using Graphon and benzene solutions of GR-S, there was little change in the amount of rubber sorbed after one hour. The intrinsic viscosity of the supernatant liquid increased initially and then decreased, up to 48 hours of shaking. For the sake of completeness, data are given on a time study of the sorption of GR-S in *n*-heptane by 1.5 grams of Vulcan-1 (Table

TABLE IV

EFFECT OF TIME OF SHAKING ON SORPTION OF GR-S (57.5 PER CENT CONVERSION) IN *n*-HEPTANE ON VULCAN-1

Time (hrs.)	Residual rubber (g./100 cc. soln.)	Rubber sorbed (g.)	Intrinsic viscostiy[a]
0	0.238	—	1.21
0.25	.119	0.119	1.15
1.0	.096	.142	1.16
2.0	.089	.149	0.98
4.0	.077	.161	.86
24.0	.068	.710	.64
40.0	.072	.166	.57

[a] Intrinsic viscosities determined in benzene.

IV). There is very little change in the amount of rubber sorbed after two hours of shaking, but the intrinsic viscosity of the residual rubber (determined in benzene solution) decreased continuously with time. This indicates that the low molecular-weight rubber is sorbed more rapidly than the higher molecular-weight polymer, but that the latter replaces the former slowly from the carbon black.

In order to test the conclusion that low molecular-weight fractions of rubber

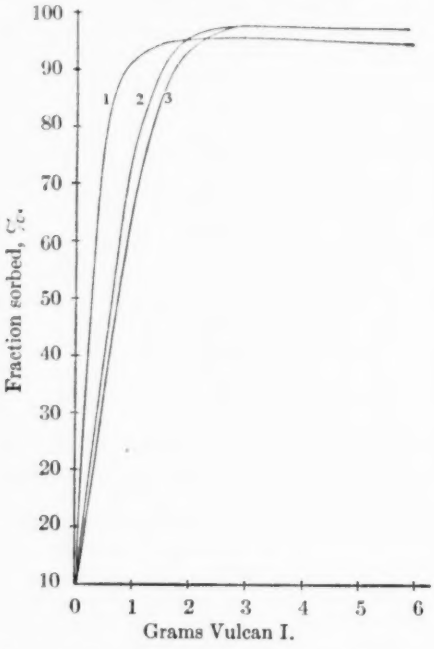

FIG. 7.—Sorption of fractions in *n*-heptane by Vulcan-1. (1) Fraction 1, $[\eta]$ = 3.69, mol. wt. 596,000; (2) Fraction 2, $[\eta]$ = 2.98, mol. wt. 433,000; (3) Fractions 3, 4, 5 and 6: Fraction 3, $[\eta]$ = 1.94, mol. wt. 229,000; Fraction 4, $[\eta]$ = 1.52, mol. wt. 159,000; Fraction 5, $[\eta]$ = 1.21, mol. wt. 113,000; Fraction 6, $[\eta]$ = 1.00, mol. wt. 85,000.

are sorbed first and are gradually replaced by the higher molecular-weight fractions, experiments of the following nature were made.

One hundred cc. of the high (or low) molecular-weight fraction was shaken with one gram of Vulcan-1 for 40 hours at 30°. The supernatant liquid was siphoned off, and 100 cc. of the low (or high) molecular-weight fraction was added to the black and shaken another 40 hours. The amount of residual rubber and the intrinsic viscosity of the solutions were determined. The solvent used for the fractions was *n*-heptane; all viscosities were measured in benzene. Some typical results are given in Table V.

It appears that when a high molecular-weight fraction is sorbed on the carbon and a low molecular-weight fraction added, there is very little change in the intrinsic viscosity of the latter. If a low molecular fraction is sorbed on the carbon and a high molecular-weight fraction added, there is a considerable de-

crease in the viscosity of the unadsorbed rubber, resulting chiefly from the displacement of some of the sorbed low molecular-weight fraction by the more strongly sorbed high molecular-weight fraction. The fact that the final values of the intrinsic viscosity reached in each member of a pair of experiments were quite different would seem to indicate incomplete reversibility of sorption. It may also be noted that somewhat greater sorption of rubber occurred in the experiments in which the high molecular weight fraction was present initially, than in those in which the low molecular weight fraction was present at the start.

Fractionation of Rubber by Sorption on a Carbon Column.—On the basis of the foregoing and the information provided by time studies of sorption, it was thought possible to fractionate a rubber sample in solution by allowing a solution

TABLE V

EXPERIMENTS WITH FRACTIONS OF HIGH AND LOW MOLECULAR WEIGHT

I. Fraction A shaken with 1 gram Vulcan-1 for 40 hours	
Fraction A, initial concn. 0.192 g./100 cc.	2.98
Rubber sorbed 0.138 gram	2.24
Remove fraction A, add fraction B, shake 40 hours	
Fraction B, initial conc. 0.235 g./100 cc.	1.00
Rubber sorbed 0.042 gram	1.14
Total amount of rubber sorbed 0.180 gram	
II. Fraction B shaken with 1 gram Vulcan-1 for 40 hours	
Fraction B, initial concn. 0.235 g./100 cc.	1.00
Rubber sorbed 0.134 gram	0.94
Remove fraction B, add fraction A, shake 40 hours	
Fraction A, initial conc. 0.192 g./100 cc.	2.98
Rubber sorbed 0.022 gram	1.60
Total amount of rubber sorbed 0.156 gram	

to flow through a column of carbon black and collecting and analyzing the eluate. This method of adsorption analysis was developed by Claesson[10] and is known as frontal analysis. For a single solute in solution, the first fractions of the eluant contain chiefly pure solvent, after which the concentration of solute increases sharply until the original value is reached.

Twenty grams of Philblack-A was placed in a glass column and retained there by a 2-cm. layer of glass wool in the bottom of the column. A carbon column, 15 cm. high and a diameter of 2 cm., was formed. Five-hundred cc. of a 0.25 per cent solution of GR-S (66 per cent conversion) in chloroform was allowed to flow through the column at a rate of about 3 cc. per minute. No external pressure was applied. Fifty-cc. portions of the eluant were collected; the concentration of the rubber and the approximate intrinsic viscosity were determined. The results are given in Table VI. Experiments with benzene and chloroform solutions, using Vulcan-1 as the adsorbent, were unsuccessful, since both the rubber and solvent were so strongly sorbed that the flow rate, even under pressure, was very small. For that reason, Philblack-A, which sorbs relatively little rubber, was selected.

TABLE VI

FRACTIONATION OF A 0.25 PER CENT SOLUTION OF GR-S BY A COLUMN OF PHILBLACK-A

Fraction	Concn. of rubber (g./100 cc. soln.)	ln $\eta r/c$
Original solution	0.247	1.34
1	0.140	0.96
2	0.200	0.96
3	0.223	1.17
4	0.230	1.13
5	0.236	1.24
6	0.236	1.30
7	0.239	1.27
8	0.240	1.27
9	0.238	1.31
At this point the liquid on top was allowed to reach the level of the adsorbent, and then pure chloroform was added.		
10	0.017	1.42

The results show that partial fractionation was obtained; after the fifth fraction the solution passed through the column substantially unchanged (*i.e.*, 250 cc. of a 0.25 per cent solution was the saturation volume for this column). From the viscosity figures it appears that the higher molecular weight rubber was more strongly sorbed. The low concentration in fraction 10 indicates that the sorbed rubber is tightly held on the black. Due to the low concentration, no great accuracy can be ascribed to the viscosity value for this fraction.

A second experiment similar to the above was made in order to ascertain whether the sorbed rubber could be desorbed from the column by a good solvent such as xylene. To obtain practically complete sorption of the rubber, Sterling-105 was selected instead of the weakly-sorbing Philblack-A. After eight portions of eluant had been collected, xylene was added to the column. It was found that of 0.469 gram of rubber sorbed, 0.296 gram or 63 per cent was desorbed from the column by 100 cc. of xylene.

Bound Rubber Formation.—The correlation between the properties of carbon blacks and their behavior in compounded rubber stocks has been widely studied. Mixing of carbon black with rubber by cold milling under conditions which do not lead to the formation of polymer gel, insolubilizes a portion of the rubber, known as bound rubber[11]. An investigation of the conditions necessary to produce bound rubber was made and some results are reported below.

Table VII gives the amount of insoluble polymer in samples of standard GR-S X-418 which had been cold-milled with equal parts of carbon black at the

TABLE VII

BOUND RUBBER IN COLD-MILLED RUBBER-CARBON MIXES

Sample	% rubber bound by 100 parts: Vulcan-1	% rubber bound by 100 parts: Sterling 105
GR-S X-418 cold-milled with 100 parts of carbon black	49.0	34.2
GR-S X-418 cold-milled, heated 4 hours at 110°	48.2	34.5
GR-S X-418 cold-milled, heated 48 hours in vacuum at 80°	51.7	38.0

Government Pilot Plant in Akron. It is seen that heating of the milled polymer up to 4 hours in air at 110° or in vacuum at 80° up to 48 hours produces practically no increase in the amount of insoluble rubber. However, heating for more than 8 hours in air at 120° produces appreciable insolubilization (gel formation, bound rubber, or oxygen vulcanization, or a combination of these). The data in Table VII were obtained by placing 0.5-gram samples in 100-mesh wire cages, which were suspended in 100 cc. of chloroform for 48 hours. The cages and contents were weighed before and after immersion. The percentage of bound rubber was calculated on the basis of rubber hydrocarbon.

In another experiment a 6-gram sample of X-418 was swollen in chloroform and an equal weight of carbon black added and mixed intimately with the rubber. The chloroform was removed under vacuum, and portions of the mixture were placed in the solvent before and after further drying *in vacuo* or after milling and drying. Solubilities were determined, using wire cages as before. Some results, given in Table VIII, were poorly reproducible, probably due to

TABLE VIII

EFFECT OF HEATING AND MILLING ON RUBBER BOUND BY VULCAN-1

Carbon added per 100 parts rubber	Method of drying	% Insoluble (on rubber hydrocarbon)	
		Not milled	Milled 10 passes
100 parts Vulcan-1	Aspirator dried only	18.9	—
	80°, vacuum, 24 hours room temp., vacuum, 24 hours	19.7 20.4	33.4 21.5

incomplete mixing of the black with the rubber on evaporation of the solvent. However, they serve to indicate that milling is not necessary to obtain bound rubber.

SUMMARY

The sorption capacities toward GR-S five commercial carbon blacks are in decreasing order: Spheron-6, Vulcan-1, Philblack-0, Sterling-105, Philblack-A. Apparently, the sorption is not related to surface area. The sorption on Vulcan-1 of GR-S from its solutions in seven different solvents or mixtures of solvents increases with decreasing solvent power for the rubber. The sorption curves of two "cold rubbers," polymerized at −10 and +5°, respectively, showed little difference from that of 50° GR-S. Previous heating of carbon black in nitrogen at 500 or 1100° increased the sorption by about 20 per cent over unheated carbon. Air-heating of carbon black at 425° did not cause a difference in the sorption from benzene solution, but produced an increase in the sorption of rubber from *n*-heptane solution. In the range 75% butadiene-25% styrene to 5% butadiene-95% styrene, there is practically no effect of the degree of unsaturation on the sorption. Polystyrene of high intrinsic viscosity exhibits a peculiar behavior with furnace blacks. Vulcan-1 sorbed microgel as well as the sol fraction from *n*-heptane solutions of GR-S containing microgel (conversion 74.7 and 81.5 per cent). There was no appreciable difference in the amount of sorption of rubber fractions having average molecular weights varying from 433,000 to 85,000. There is little change in the amount sorbed after two hours of shaking, but the intrinsic viscosity of the

residual rubber decreases with time. The low molecular-weight rubber is sorbed more rapidly, but is slowly replaced by the more tightly sorbed high molecular weight fraction. Partial fractionation of a rubber sample can be achieved by allowing the rubber solution to flow through a column of weakly sorbing carbon black. A large portion of the sorbed rubber can be recovered from the column by washing it with a good solvent such as xylene. Bound rubber is produced by intimate mixing of equal parts of carbon black and rubber swollen in chloroform, when the mixture is dried in vacuum at 80° or at room temperature. Milling is not essential to get bound rubber.

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[9] Actually the inherent viscosity $= \ln \eta_r/c$ was determined, where η_r is the relative viscosity and c is the concentration in grams per 100 cc. However, at the concentrations used, this is a close approximation to the intrinsic viscosity. The average molecular weights were calculated from the relation: $\log M = 4.93 + 1.49 \log [\eta]$, where M is the molecular weight and $[\eta]$ is the intrinsic viscosity (*cf.* French and Ewart, *Ind. Eng. Chem. Anal. Ed.* **19**, 165 (1947); Scott, Carter, and Magat, *J. Am. Chem. Soc.* **71**, 220 (1949).
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STUDIES IN THE DISPERSION OF SRF CARBON BLACK IN BUTYL RUBBER *

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The vital function of carbon black as a reinforcing agent for natural as well as synthetic rubber is familiar to all rubber technologists. As such, the degree and manner of its dispersion is a matter of great importance, and has been the subject of much speculation and experimentation within the industry. For example, the adverse effect of poor carbon black dispersion on tire-tread wear has long been recognized, and much effort has been expended to achieve optimum dispersions. In fact, the maximum in physical properties of any compound are realized only with the best possible dispersions.

It is also acknowledged that many factory processing problems are related to carbon black dispersion. Plasticity, processing behavior, and vulcanization rate may be affected by variation in dispersion. The behavior of rubber compounds in milling, extrusion, and calendering operations is influenced by variations in carbon black dispersion. For example, a coarse dispersion frequently results in porous extrusions. Likewise, the important property of tack or cohesiveness may be adversely affected by poor dispersion, expecially in synthetic rubber stocks.

Examples of such problems may be cited from early experience in the commercial development of Butyl-rubber inner tubes. Probably most of these difficulties can be discounted on the basis of limited experience with a new material. However, a frequent complaint was that unvulcanized tubes were readily distorted during fabrication. Thin spots at the folds were the most common manifestation of this phenomena. Another source of trouble was in the butt-splicing operation, where the ends of the flat tube were joined.

These and similar problems suggested that this new synthetic product was not uniform from one lot to another. Exhaustive laboratory and factory scale experiments, however, failed to substantiate this contention. In fact, it was clearly demonstrated that many difficulties, such as those just mentioned, could be traced to variables in factory processing operations. One of the most important of these variables was the degree of dispersion of the carbon black.

The significance of carbon black dispersion is, therefore, evident. This paper is primarily concerned with new techniques for measurement of carbon black dispersion by means of the electron microscope and parallel-plate plastometer. The electron micrographic results are correlated with plastometric measurements.

EXPERIMENTAL PROCEDURES

Preparation of the compounds.—Experience suggested that variations in carbon black dispersion could be produced in the laboratory by simple and controllable changes in mixing equipment and techniques. Accordingly, five

* Reprinted from the *Rubber Age* (N. Y.), Vol. 70, No. 4, pages 457–463; January 1952.

separate batches of a carbon black-synthetic rubber stock were prepared on a 6 × 12-inch laboratory mill. GR-I-15 was selected as the polymer, to which 50 parts of a semi-reinforcing furnace black was added. The only variables introduced were the mill roll settings and, consequently, batch size. The roll clearances varied from 0.010 to 0.070 inch and the batch weighs from 75 to 600 grams. This appeared to be the simplest manner in which substantial differences could be obtained in the amount of work or shearing action performed on a compound under controlled conditions.

Two simple precautions were necessary to allow the mill-nip setting to be the determining factor in the dispersion of pigment particles into the polymer. First, the batch size had to be kept at a minimum so that excessive working of the stock did not take place in the mill bank. Second, the usual blending and cutting of the batch on the mill had to be avoided for similar reasons. The principal variable, therefore, became the gap between the two mill rolls. The mixing was done on a cold mill, and was continued only as long as was necessary to completely incorporate the carbon black into the polymer.

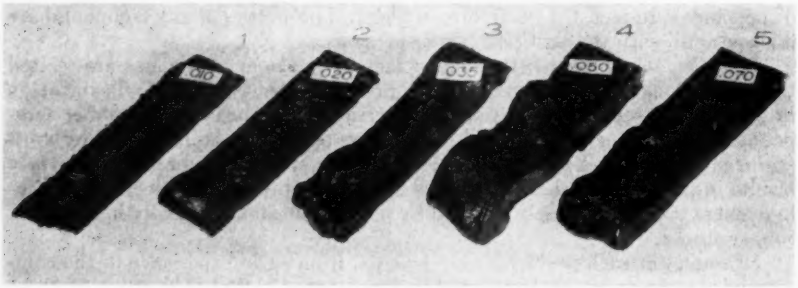

FIG. 1.—One-inch wide strips of Butyl-carbon black compounds cut from mill slabs soon after mixing on a conventional 6 × 12-inch laboratory mill. Mill-nip settings are indicated by the figures superimposed on the strips.

The compounds so prepared contained only polymer and carbon black pigment; softeners, processing aids, and other modifiers were avoided. In this way it was possible to obtain a series which varied only in the degree of carbon black dispersion.

These compounds (Figure 1) had some differences which were immediately discernible. The compounds prepared on the tightest mills appeared to be blacker and more shiny than those mixed on more open mills. The former had better building tack and were less porous. Compound No. 5 was found to have the poorest dispersion of the series. It would be expected to have the poorest extrusion, forming, and splicing properties. Conversely, the first compound would be expected to process very well in these respects.

In all probability, the five compounds represented the range in degree of carbon black dispersion which might be experienced in commercial processing operations.

The differences between the compounds became more conspicuous when they were prepared as dilute supensions (0.0068 per cent by weight) in petroleum naphtha (Figure 2). The photograph of these suspensions was taken after they had been allowed to settle for three days. Photometric measurements of these suspensions were obtained, before settling, by means of a Diller colorimeter. The data are shown in Table III.

Several other series of compounds were prepared by the variable mill-nip technique, and differences were observed in their properties comparable to those described above. It was apparent, then, that a simple, reproducible method had been found for obtaining varying degrees of black dispersion in Butyl rubber. It was, therefore, desirable to consider other, more accurate, methods of studying such dispersions. The instruments chosen for this work were the electron microscope and the parallel-plate plastometer. With the former it is possible to make very accurate observations on the degree of dispersion or disaggregation of carbon blacks in admixture with a polymer. On the other hand, precise measurements of physical properties of the unvulcanized state are possible with the parallel-plate plastometer. Both methods have been used in studying the carbon black dispersions. The results obtained are discussed in the balance of this paper.

Electron microscope examination.—The electron micrography of colloidal carbon in uncured and vulcanized rubber appears to be a subject that has not

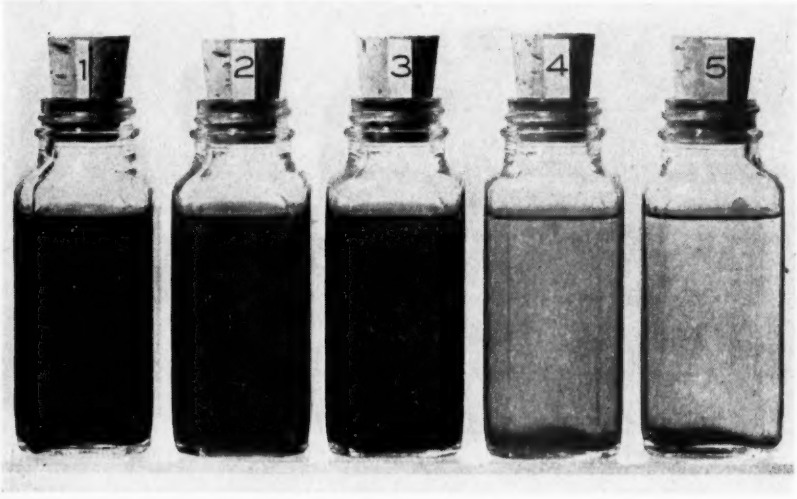

FIG. 2.—Appearance of dilute suspensions of the five compounds in petroleum naphtha after standing for three days.

been given very wide coverage in the literature. The most comprehensive work on this problem seems to have been done by Ladd[1]. He offers three techniques for the electron micrography of carbon-rubber specimens:

1. The *rub-out technique*, wherein the uncured rubber is "rubbed out" on a glass-supported Formvar membrane. The membrane is subsequently removed from the glass and mounted on the specimen screen.

2. The *replica method*, by which a replica is made of the fractured surface of a rubber black.

3. The *vulcanizing method*, in which a small block of uncured rubber mix is placed, under high pressure, between a convex and a plane surface, and then vulcanized. The thin pressed-out section of the block is subsequently used as an electron-microscope specimen.

The authors felt that none of these techniques would give a true picture of

the degree of dispersion. The physical work necessarily applied to the compound by methods 1 and 3 undoubtedly causes further breakdown of carbon-black agglomerates, while the replica technique, limited as it is to the representation of a single plane, can give no measure of carbon agglomeration.

Previous experience with the dispersion of reinforcing blacks for electron-microscope examination led to the firm conviction that the extensive agglomeration found in these blacks is not due to any unusual attraction between particles, but rather is due to a physical bonding of the particles during their formation. Assuming this concept to be correct, the function of a mill or Banbury mixer

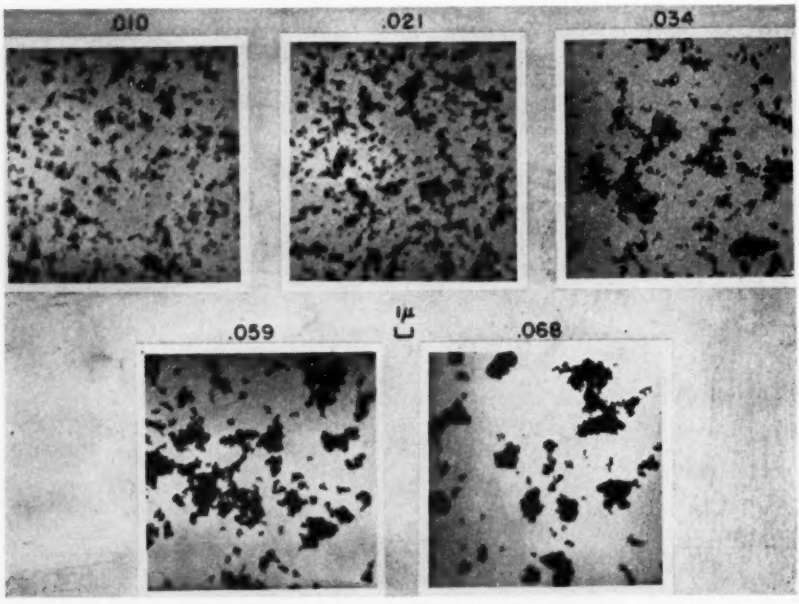

FIG. 3.—Electron micrographs of Butyl-carbon black dispersions, December, 1949.

can be divided into two distinct parts: (1) distribution of the carbon black uniformly throughout the mass of rubber, and (2) reduction, by fracture, of the size of the bonded agglomerates.

Although these two functions undoubtedly occur simultaneously, they can, for purposes of study, be thought of as separate and distinct. The first function, which will be referred to as distribution, can be easily measured by analyzing samples taken from various parts of the mix. The second function, which will be called dispersion, was the one studied by means of the electron microscope.

Considering the large amount of effort necessary to reduce the size of bonded agglomerates by working in a viscous medium, and the fact that it is practically impossible to reduce their size by simply shaking in a liquid medium, it was felt that a solution technique, similar to that used by von Ardenne[2] or Hall[3], would give the most satisfactory picture of dispersion. Inasmuch as the distribution of carbon black throughout the mass of a mix can be evaluated, as pointed out above, by a separate means, the only factor to be measured with regard to the

dispersion of the black is the degree of breakdown of the bonded agglomerates. Therefore, dissolving the rubber from around the agglomerates and redispersing them in a single plane so that they might be viewed with the electron microscope, appeared to offer the simplest method of evaluating breakdown.

The technique used in the preparation of the electron microscope specimens was as follows.

1. One per cent solutions of the compounds to be examined were prepared by mechanically shaking a weighed portion of the compound in the proper volume of heptane. Immediate and continued shaking is essential until all of the compound is dissolved because, if the undissolved compound is allowed to stand quietly in the heptane, swelling occurs, and this markedly increases the amount of agglomerate breakdown. If, on the other hand, the sample is shaken, the rubber dissolves at a more rapid rate than the heptane can diffuse into the rubber causing swelling.

2. A glass microscope slide is dipped about $\frac{2}{3}$ of its length into 0.1% Formvar (polyvinyl formal resin) in ethylene chloride solution and allowed to dry in a vertical position.

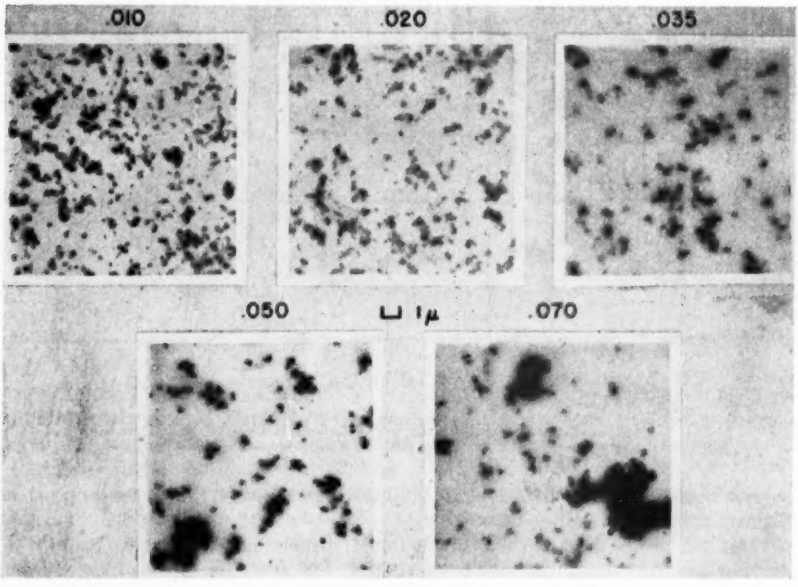

FIG. 4.—Electron micrographs of Butyl-carbon black dispersions, December, 1950.

3. The Formvar-coated slide is next dipped to about $\frac{1}{2}$ its length in the freshly shaken heptane solution of the compound. Again it is allowed to dry in a vertical position.

4. The sharp edges of the slide are scraped with the side of a needle in order to cut through the rubber and Formvar films, and then the double film is floated off on water. A portion of the floating film is mounted on a specimen screen in the usual manner.

The proper interpretation of micrographs of specimens prepared by the above technique must be compatible with the limitations of that technique.

For instance, the amount of carbon black in any one field has no significance. The only useful information that can be derived from these micrographs is particle and agglomerate size. The formation of a rubber film simultaneously with evaporation of the heptane has the advantage of keeping the carbon particles and agglomerates in a well dispersed condition. A minor amount of flocculation does occur, but it is possible to differentiate between a floc and a bonded agglomerate. The individual particles in a floc are quite distinct and are obviously in the same plane, while the opposite is true of the bonded agglomerates. The particles in the latter are chained in three dimensions causing them to mask one another. These agglomerates generally appear as dark ir-

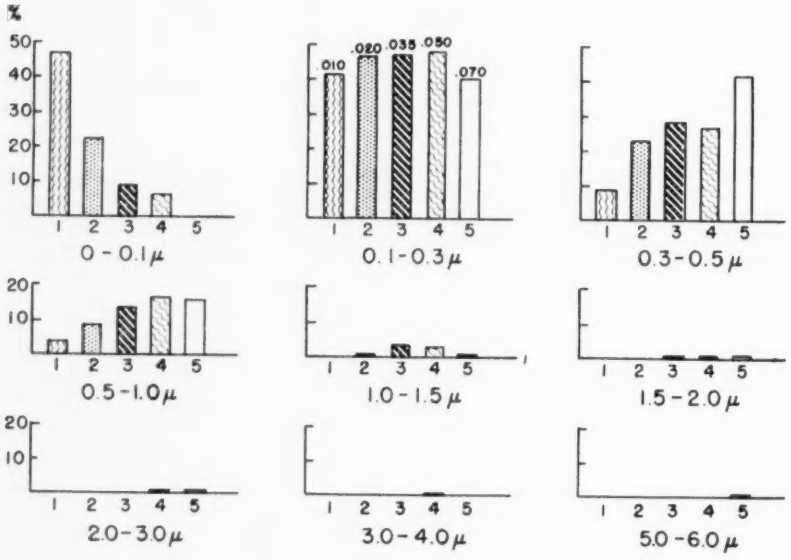

FIG. 5.—Agglomerate size distribution of Butyl-carbon black dispersion. Data are based on a statistical analysis of the electron micrographs shown in Figure 4.

regular masses, with little or no detail appearing except at the edges, as seen in Figures 3 and 4.

The preparation of carbon black-Butyl dispersions by the technique of varying mill-nip openings has been carried out on a number of occasions. Characteristic electron micrographs of such dispersions are shown in Figures 3 and 4. The correlation between agglomerate size and mill setting is quite evident. In the best dispersions, discrete particles of the SRF black are discernible and measurements indicate that they are 0.06 to 0.10 micron in diameter. In coarser dispersions, large clumps or aggregates are seen with diameters as great as 5 or 6 microns. Such clusters contain 100,000 or 200,000 individual particles. Their presence may result in "starvation of reinforcement," and has a profound effect upon opacity of dilute solutions.

A statistical analysis has been made on the agglomerate size distributions of a series of five dispersions. These data are shown on the bar graphs in Figure 5. The data were obtained by counting and measuring between 200

and 300 agglomerates on suitable electron-micrograph prints. The actual values are shown in Table I.

Several important facts may be noted from these data. By far the largest occurrence of 0.0–0.1μ particles is in the 0.010-inch milled stock, and the frequency of these smallest particles falls off sharply as the mill opening is increased. Likewise, the very largest clumps occur only in compounds prepared on the more open mills. There are no 0–0.1μ particles in the 0.070-inch gage stock. The frequency in the 0.1–0.3μ class is remarkably uniform for all stocks. In the next larger group, 0.3–0.5μ, a definite discontinuity in the frequency occurs with the No. 4 stock which was mixed on a 0.050-inch mill. Further reference will be made to this point.

The electron microscope has thus provided excellent confirmation of the expectation that large differences in the degree of dispersion exist in the five

TABLE I

AGGLOMERATE SIZE DISTRIBUTION

Stock	1		2		3		4		5	
GR-I-15	50		100		200		300		400	
SRF Black	25		50		100		150		200	
Mill setting (inch)	0.010		0.020		0.035		0.050		0.070	
Time on mill (minutes)	4		3		4		4		5	
No. counted	271		242		239		255		203	
Average size (microns)	0.17		0.26		0.35		0.39		0.46	
Distribution	No.	%	No.	%	No.	%	No.	%	No.	%
0–0.1μ	126	46.5	54	22.3	21	8.8	16	6.3	0	0
0.1–0.3μ	112	41.3	113	46.7	112	46.9	122	47.8	82	40.4
0.3–0.5μ	23	8.5	54	22.3	67	28.0	67	26.3	83	40.9
0.5–1.0μ	10	3.7	20	8.3	31	13.0	41	16.1	31	15.3
1.0–1.5μ	—	—	1	0.4	7	2.9	6	2.4	1	0.5
1.5–2.0μ	—	—	—	—	1	0.4	1	0.4	2	1.0
2.0–3.0μ	—	—	—	—	—	—	1	0.4	2	1.0
3.0–4.0μ	—	—	—	—	—	—	1	0.4	0	0
4.0–5.0μ	—	—	—	—	—	—	—	—	0	0
5.0–6.0μ	—	—	—	—	—	—	—	—	2	1.0

compounds under examination. It remains to be demonstrated that these differences result in significant differences in the physical properties of such compositions, differences which might correlate with important processing variables in the commercial utilization of such compositions.

Parallel-plate plastometer studies.—To measure the physical properties of these Butyl-black compositions in the unvulcanized state, use was made of the parallel-plate plastometer, an instrument which measures the viscous and elastic behavior of polymers in fundamental units. It was selected as a means of measuring the physical properties of the unvulcanized compounds because of its convenience, availability, simplicity of operation and sensitivity. This instrument was described by Dienes and Klemm.[4] The instrument is similar to the commonly used Williams plastometer, but is superior in these respects: (1) greater freedom from frictional effects; (2) better temperature control; (3) greater latitude in the range of applied load. Measurements are made of the deformation *vs.* time behavior of polymer samples under compression, and the data are treated in the light of Stefan's analytical development of fluid flow between parallel plates. Stefan has shown that, in cases where a viscous fluid does not completely fill the space between the plates, a material exhibiting Newtonian behavior should give a linear relation between the inverse fourth

power of the plate separation, h, and the time of deformation, t. The final result can be written:

$$1/h^4 = 8\pi Ft/3\eta V^2 + C$$

where h = distance between plates
F = applied force
V = volume of specimen
η = viscosity coefficient
t = time
and C is an integration constant.

Dienes and Klemm showed that for certain polymers, after an initial time interval, the plot of $1/h^4$ against t becomes linear in accordance with the above

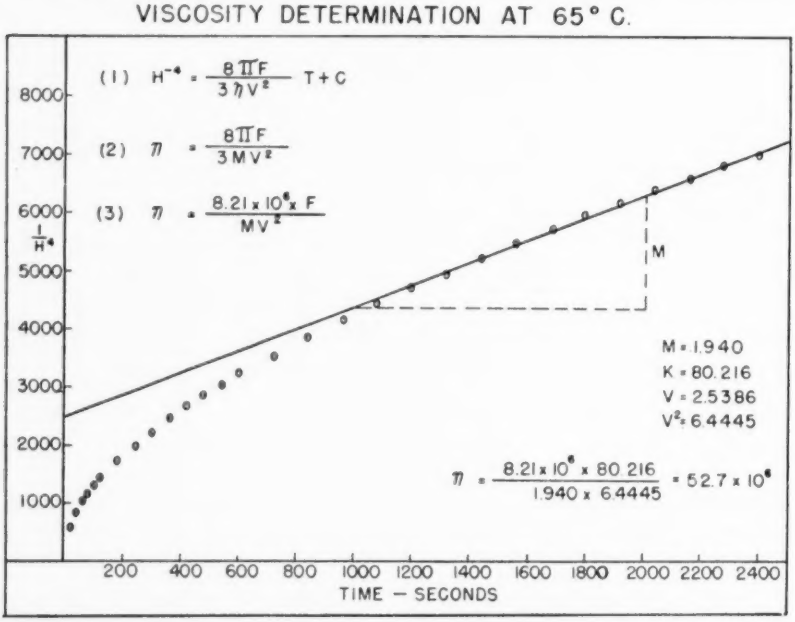

FIG. 6.—Calculation of the viscosity of a polymer-pigment system, determined at 65° C, by means of the parallel-plate plastometer. Dienes and Klemm have shown that, under certain conditions, Stefan's equation (1) for fluid flow between parallel plates is applicable to polymeric systems. The equation may then be expressed as in (3), and the viscosity calculated therefrom.

equation, and the dependence on the applied force is likewise in agreement. In other words, after an initial period in which elastic deformation is predominant, the flow of the polymer is simply viscous and follows Newtonian behavior. A typical flow curve is shown in Figure 6, the method of calculation also being indicated.

Viscosity data were obtained on two sets of carbon black-Butyl dispersions prepared and tested about a year apart. Data for both sets of stocks are shown in Table II. Included in these data are values for unpigmented polymer both before and after milling for at least seven minutes on a cold tight mill. The reduction in viscosity during such an operation is negligible, and it may be

assumed that the large differences in viscosity indicated for the carbon black loaded compounds are actually due to differences in the degree of dispersion.

One of the interesting facts to be pointed out here is that the poorest dispersion has the highest viscosity and the best dispersion has the lowest viscosity. This is consistent with commercial experience in remilling of Butyl stocks, where the additional working lowers the Mooney viscosity more than can be expected as a result of polymer breakdown alone. It is also consistent with current theoretical work by Guth[5], and other investigators, who have found a shape factor to be of importance in calculating viscosities of carbon black-polymer systems.

It is also interesting to point out the reproducibility of such viscosity determinations. In most cases these values check quite closely for stocks prepared

TABLE II

VISCOSITY MEASUREMENTS OF CARBON BLACK DISPERSIONS
(50 Parts SRF in GR-I-15)

	1949		1950	
	Mill setting	Viscosity $\eta(\times 10^{-6})$	Mill setting	Viscosity $\eta(\times 10^{-6})$
Pure-gum (before milling)	—	18.5	—	20.3
		19.6		20.5
				21.8
Pure-gum (after milling)	0.010	18.7	0.010	18.7
		18.9		19.3
				19.8
C'P'D. 1 75 grams	0.010	46.3	0.010	38.5
		48.6		40.6
2 150 grams	0.021	46.1	0.020	47.0
		50.6		48.2
				48.6
3 300 grams	0.034	51.6	0.035	54.6
		55.6		54.7
4 450 grams	0.059	59.8	0.050	50.4
		65.4		51.2
				52.2
5 600 grams	0.068	69.1	0.070	67.2
		71.7		71.1

in similar manner some time apart. There is very good agreement among several determinations on one sample. These data indicate that this method of viscosity determination is quite accurate and reproducible.

An apparent anomaly occured in the case of the No. 4 stock mixed in December, 1950, on a 0.050-inch-gage mill. The viscosity data appeared to be out of line with the general trend. It will be noted that the previous mixing of this 450 gram batch was done on a considerably wider mill, 0.059-inch nip opening. On examination, it turns out that this is undoubtedly a significant difference in the milling conditions. Not only will more grinding take place between the rolls, but a substantially larger bank of stock is present in which additional fracturing of the carbon black can take place because of the deformation and recovery of the polymer as it is worked on the mill.

As pointed out earlier in the discussion of agglomerate size distributions, there is a discontinuity in the frequency of occurrence of 0.3–0.5μ particles for the No. 4 stock (0.050-inch mill mix). This condition is consistent with the viscosity relationships.

The correlation of three different properties of Butyl-carbon black systems is given in Table III. The light transmission data were obtained with a Diller

TABLE III

CARBON BLACK DISPERSIONS
(50 Parts SRF in GR-I-15)

Mill setting (inches)	% light transmission (0.0068% sol'n.)	Average agglomerate (microns)	Viscosity ($\times 10^{-6}$ poises)
0.010	20	0.17	39.6
0.020	25	0.26	47.9
0.035	57	0.35	54.6
0.050	53	0.39	51.3
0.070	60	0.46	69.2
GR-I-15 (not milled)			20.9
GR-I-15 (milled 7′, 0.010″ setting)			19.2
GR-I-70 (not milled)			54.5

Colorimeter, using suspensions containing 0.0068 per cent solids. These values appears to be quite consistent with viscosity data as well as with agglomerate size distribution (Figure 5). Comparative data are also shown for two pure-gum polymers (GR-I-15 and GR-I-70). The Mooney viscosity of these two polymers varies approximately 35 points when tested at 212° F. The difference between the two extremes of carbon black dispersion appears to be of the same order of magnitude.

DISCUSSION

It has been well established in commercial practice that the processing characteristics of a Butyl compound are improved as the dispersion of carbon black is improved. By this is meant that the extruding, forming, and splicing operations are performed more easily, and with fewer defects. A finer dispersion gives a more homogeneous composition, which is relatively free of porosity, and which can be stretched and shaped more uniformly. Poor dispersions tend to give rough uneven surfaces, which are more easily deformed, developing localized thin spots. It is to be expected that a firm, homogeneous stock will be easier to splice than a nonuniform material of greater viscosity.

It also seems reasonable to expect that relatively large irregular agglomerates would occlude air, gases or moisture more readily than a fine divided black pigment. If this is true, it is easy to understand why poorly dispersed carbon black stocks would frequently become porous upon extrusion. The occluded gases or moisture would expand during such an operation (usually carried out between 200° and 275° F), forming a cellular or spongy structure.

It is even more evident that large agglomerates, which are more loosely held by the polymer throughout which they are distributed, will settle out of solution quite readily. Thus it may be expected that cements made of poorly dispersed stocks will settle out and possess low adhesive strength.

In connection with the data and discussion presented above, it is interesting to note two papers, relating to dispersion of carbon black in rubber, which have recently been published. In a study of the "Electrical Resistivity of Various Carbon Blacks in Natural, GR-S, Cold, and Butyl Rubbers," Sperberg, Popp, and Biard[6] found that "Butyl rubber is markedly superior to the other rubbers in contributing to excellent conductivity in black-loaded compound, but is similar to the other rubbers in gum stocks. The trend in results is prob-

ably due to varying black dispersion in each of the rubbers. Since Butyl rubber is quite thermoplastic, less grinding action is exerted by this rubber than by the other rubbers and hence the black dispersion is poorer." Poor dispersion would account for good electrical conductivity.

The authors conclude "that the degree of milling of rubber-carbon black mixes has a major effect upon electrical resistivity of intermediate and large particle size blacks but has a relatively negligible effect upon fine particle size furnace and channel blacks. . . . Butyl rubber imparts excellent conductivity characteristics when reinforced with MAF black, which should contribute to lower static charge accumulation on vehicles equipped with Butyl rubber inner tubes."

In investigation by Dannenberg, Jordan and Stokes[7], on the "Effect of Mechanical Aggregation on the Dispersion Characteristics of Carbon Black," the authors reach similar conclusions regarding the dispersion of carbon black in Butyl. Using light transmission and electrical conductivity measurements, they concluded "that the main factor responsible for the dispersion of carbon blacks is the nerve or elastic property of the medium, which causes the disintegration of the carbon aggregates by the continual processes of deformation and elastic recovery or swelling of the raw stock during mixing and milling." In an interesting series of experiments, they demonstrated that the dispersion of carbon black in Butyl can be markedly improved by the familiar Polyac reaction. Heat treatment of Butyl with Polyac, a cross-linking agent, for five minutes in a Banbury at 300 to 330° F, increases the toughness and nerve of this polymer. This increased nerve greatly improves carbon black dispersion. It was also shown that mere increase in viscosity, alone, is insufficient to influence dispersion.

In the present work, the authors have demonstrated that the degree of black dispersion in Butyl can also be altered by simple mechanical changes in the milling or mixing conditions. A new technique for measuring such differences by use of the electron microscope has been described. Such results correlate well with simple light transmission measurements. It is suggested that differences in dispersion have an important relationship to processing characteristics. Finally, the measurement of physical properties of unvulcanized carbon black systems has been accomplished by means of the parallel-plate plastometer. The results obtained on this instrument are in good agreement with electron micrograph and light transmission observations. It is suggested that such techniques provide valuable tools for research in the field of pigment reinforcement of elastomeric materials.

SUMMARY

A simple method is described for producing different degrees of carbon black dispersion in elastomers under controlled laboratory conditions. Careful selection of milling conditions has made possible the preparation of stocks possessing variations in degree of dispersion, comparable to the wide differences noted in practice.

A new technique is described for studying these carbon black dispersions in rubber by means of the electron microscope. Such studies show large differences in degree of agglomeration of carbon black in compounds made under simple variations of conditions. Representative electron micrographs are shown. Good correlation is obtained between these micrographs and light transmission measurements of dilute solutions of the compounds. Such photo-

metric analysis provides a simple method for the measurement of carbon black dispersion in research or control work.

The observed differences in degree of dispersion have an effect on the physical properties of the unvulcanized compounds. This effect was observed by means of the parallel-plate plastometer. The viscosity values obtained with this instrument show a direct correlation with electron micrographic observations.

Some of the practical and theoretical implications of this study are discussed with reference to recent work in this field by other investigators.

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OZONE AND SUNLIGHT EFFECT ON AGING OF CARBON BLACK VULCANIZATES *

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The effect of both natural and artificial sunlight aging and ozone exposure on carbon black-loaded rubber vulcanizates, as used in tire treads, tire sidewalls, and various mechanical rubber goods products, is deleterious. Exposure to sunlight and ozone accelerates the deterioration of the physical properties of the rubber compound, and checking and cracking develop. Williams[1], while studying the oxidation of rubber exposed to light, was probably the first to point out the effect of ozone on rubber. Van Rossem and Talen[2] found that the presence of light is not essential in the formation of cracks in a vulcanizate. Depew[3] studied the surface deterioration of rubber in sunlight under varied mechanical stresses. Norton[4] in, his investigation on "The Action of Ozone on Rubber and Other Materials," found that, in order to specify the life of a rubber composition, the mechanical stress as well as the ozone concentration in the surrounding atmosphere must be known. Nellen *et al.*[5] found that the degree of deterioration of tires in storage from ozone attack varies according to the geographic location, the construction material and ventilation of storage facilities, subjected stress during storage, and product covering.

During World War II, shortages of paper and manpower resulted in practically all tires being marketed unwrapped. With the low tire inventories that existed and the rapid turnover, aging problems were minimized. Since considerable savings were effected thereby, manufacturers continued the practice of omitting wrappings on tires long after the war. As the pent-up demand became satisfied and inventories began to build up, cracking became evident in unwrapped storage. Rubber technicians, confronted with this cracking condition in addition to the ever-existent sun checking problem, began to explore the behavior of the synthetic butadiene-styrene polymers and the new type of furnace blacks that were coming into widespread use. It was theorized by some rubber technicians that these new furnace blacks, with their high modulus properties, were conducive to greater checking and ozone cracking characteristics, compared to conventional gas blacks, which exhibit lower modulus properties. Hence this investigation was initiated approximately one year ago to study the effects, if any, of various types of carbon blacks on checking and ozone cracking of natural and synthetic rubber vulcanizates under static testing conditions.

METHOD

Typical tire-tread compounds of both natural rubber and low-temperature polymer X-478, 41° F, with and without antioxidants, employing HAF, EPC, MAF, HMF, and SRF types of blacks were studied. Samples 0.5 inch wide

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by 6 inches long were prepared from ASTM tensile test sheets and were subjected to ozone and sunlight aging while under an elongation of 12.5 per cent. Another series of samples of like dimensions were simultaneously tested while under a 180 degree bend. The specimens were subjected to outdoor exposure for 32 days in the instance of low-temperature polymer and 63 days for natural-rubber vulcanizates. Weather aging tests were conducted in Akron, Ohio, during the months of April and May, 1950. In the case of ozone aging, the specimens were prepared and arranged in the same manner as the weather aged specimens. The specimens for ozone aging were placed in an enclosed box similar to that developed by Baruth[6] in his study pertaining to discoloration of white sidewall compounds and the generated ozone effect by ultraviolet light.

TABLE I

NATURAL RUBBER PHYSICAL TEST DATA

	Recipes by carbon black type (parts)				
	HAF	EPC	MAF	HMF	SRF
Smoked sheet	100	100	100	100	100
HAF black (Philblack O)	50	—	—	—	—
EPC black (Wyex)	—	50	—	—	—
MAF black (Philblack A)	—	—	50	—	—
HMF black (Statex 93)	—	—	—	50	—
SRF black	—	—	—	—	50
Zinc oxide	5	5	5	5	5
Stearic acid	3	3	3	3	3
Softener	3	3	3	3	3
Accelerator[a]	0.5	0.65	0	0.5	0.5
Sulfur	2.5	2.7	2.5	2.5	2.5
Antioxidant[b]	1	1	1	1	1

Physical test data stress strain (original)

Minutes cure at 280° F					
	300% Modulus (lb./sq. inch)				
10	980	400	1070	430	270
20	1600	1120	1708	1000	1080
30	2060	1580	2150	1310	1410
40	2170	1670	2250	1580	1470
60	2170	1830	2230	1620	1420
90	1950	1650	2180	1580	1270
	Tensile at break (lb./sq. inch)				
10	3480	1410	2800	840	900
20	4230	4230	3910	3750	3900
30	4530	4540	4020	3880	3840
40	4460	4480	3820	3680	3840
60	3920	4300	3720	3610	3680
90	3890	4220	3670	3660	3320
	Ultimate elongation (%)				
40	540	605	470	565	580
60	555	565	465	540	570
90	500	585	480	555	550
	Shore hardness				
40	64	63	63	58	58
60	67	67	65	63	61
90	66	66	63	62	60

[a] Santocure.
[b] Thermoflex.

Exposure time was 8 to 12 hours, in the instance of low-temperature polymer compounds, and 132 hours for the natural rubber compounds. The distance between the surfaces of the specimens and the lamps was 7 inches.

RESULTS

Table I shows the stress-strain properties and Shore hardnesses of the five different carbon blacks in natural rubber. Table II shows the stress-strain properties and Shore hardnesses of the five different carbon blacks in low-temperature polymer.

The subsequent figures show the effect of outdoor and ozone exposure when a number of commercially available antioxidants and inhibitors are incorporated in a compound. Talc was rubbed into the cracks of the exposed rubber samples to obtain a better pictorial effect. Figure 1 shows five natural-rubber vulcanizates containing 50 parts each of different types of carbon black as loading after 63 days of weather exposure. Cure time was at 280° F, and all compounds contained 1 part of Thermoflex A. Checking was slight and equal for all the specimens. Figure 2 reflects the same compound comparisons as in Figure 1.

TABLE II

X-478 COLD RUBBER PHYSICAL TEST DATA

	Recipes by carbon black type (parts)				
	HAF	EPC	MAF	HMF	SRF
GR-S X-478	100	100	100	100	100
HAF black (Philblack O)	50	—	—	—	—
EPC black (Wyex)	—	50	—	—	—
MAF black (Philblack A)	—	—	50	—	—
HMF black (Statex 93)	—	—	—	50	—
SRF black	—	—	—	—	50
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Softener	10	10	10	10	10
Accelerator[a]	1.2	1.5	1.2	1.2	1.2
Sulfur	1.75	1.75	1.75	1.75	1.75
Physical test data stress strain (original)					
Minutes cure at 292° F	300% Modulus (lb./sq. inch)				
40	1370	620	1560	860	620
60	1560	860	1760	1000	730
90	1650	1010	1760	1030	740
	Tensile at break (lb./sq. inch)				
40	3280	3100	2470	2470	2160
60	3480	3400	2830	2600	2360
90	3660	3280	2720	2740	2020
	Ultimate elongation (%)				
40	560	770	445	680	740
60	550	705	495	635	725
90	555	645	455	625	645
	Shore hardness				
40	64	61	64	57	55
60	66	63	64	58	56
90	66	63	64	59	56

[a] Santocure.

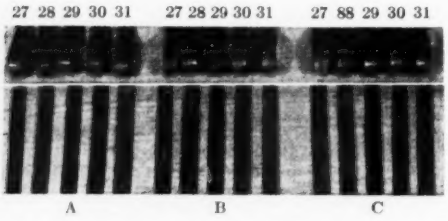

FIG. 1.—Cracking of natural rubber after 63 days' exposure to natural sunlight.

A. Cured 40 minutes.
B. Cured 60 minutes.
C. Cured 90 minutes.
27. MAF.
28. HAF.
29. EPC.
30. SRF.
31. HMF.

In this instance, also, only slight checking was detected, and an approximately equal degree of checking was found on the five vulcanizates after 132 hours of exposure to ultraviolet ozone generation. There is indication of a slight superiority in the MAF black when under stress; however, the 180-degree-bend

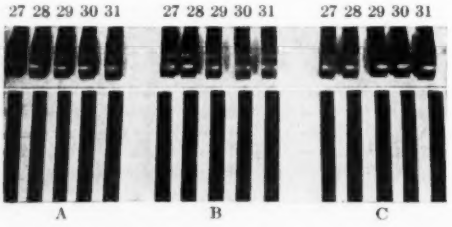

FIG. 2.—Cracking of natural rubber after 132 hours' exposure to ultraviolet lamps.

A. Cured for 40 minutes.
B. Cured for 60 minutes.
C. Cured for 90 minutes.
27–31. See Figure 1.

samples show that the talcing of the stressed specimens may have influenced their photographic reproduction.

Figure 3 compares the HAF, EPC, and MAF types of blacks in natural rubber at a 50-part loading (280° F cure) with various antioxidant and inhibitor

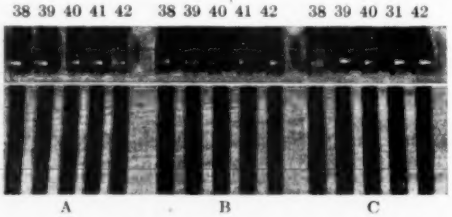

FIG. 3.—Cracking of natural rubber after 63 days' exposure to natural sunlight.

A. Cured for 40 minutes.
B. Cured for 60 minutes.
C. Cured for 90 minutes.

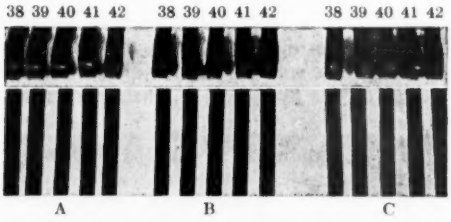

FIG. 4.—Cracking of natural rubber after 132 hours' exposure to ultraviolet lamps.

A. Cured for 40 minutes.
B. Cured for 60 minutes.
C. Cured for 90 minutes.

combinations, and a lower sulfur content, with acceleration adjustment for the sulfur reduction. The formulas were as follows:

Compound	38 (MAF)	39 (HAF)	40 (EPC)	41 (MAF)	42 (MAF)
Accelerator	0.50	0.50	0.65	0.50	0.75
Sulfur	2.50	2.50	2.70	2.50	1.75
Santoflex AW	1.50	1.50	1.50	1.50	1.50
Santoflex BX	1.00	1.00	1.00	1.00	1.00
Heliozone	—	—	—	1.00	1.00

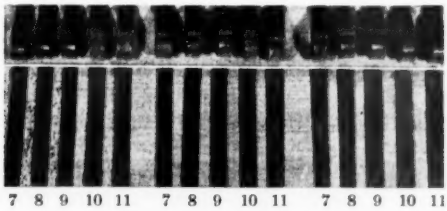

FIG. 5.—Cracking of low-temperature polymer, X-478, after 32 days' exposure to natural sunlight.

7. MAF.
8. HAF.
9. EPC.
10. SRF.
11. HMF.

Observations show only slight checking and equality in the degree of checking on the vulcanizates after 63 days of exposure. Figure 4 compares the same vulcanizates as Figure 3. Again, only slight to mild checking was detected, to an approximately equal degree when the vulcanizates had been exposed to ultraviolet light for 132 hours.

FIG. 6.—Cracking of low-temperature polymer, X-478, after 8 hours' exposure to ultraviolet lamps.

7. MAF.
8. HAF.
9. EPC.
10. SRF.
11. HMF.

The resistance of low-temperature polymer compounds to ozone was next investigated, as shown by the Figures 5 to 12, inclusive. Cure for all of the samples was at 280° F. The various results obtained are briefly analyzed. Figure 5 is a comparison of the five types of blacks under investigation in low-

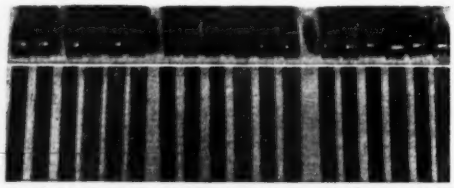

FIG. 7.—Cracking of low-temperature polymer, X-478, after 32 days' exposure to natural sunlight.

temperature polymer X-478 at 50-part loadings, without added antioxidant (above that already contained in the polymer as a stabilizer). The degree of checking is pronounced in all specimens shown in this figure and equal for the different types of blacks when exposed for 32 days to outdoor exposure. Figure 6 compares the same vulcanizates as in Figure 5. The distinguishing effect of ozone cracking is apparent in this picture; a slight superiority is shown by the HAF and EPC blacks when exposed to the ultraviolet light generated, and the number and depth of checks and (or) cracks are compared for all cures in the stressed and 180-degree bend specimens. In both Figures 5 and 6, the five samples on the left were cured for 40 minutes, the five in the center for 60 minutes, and those on the right for 90 minutes.

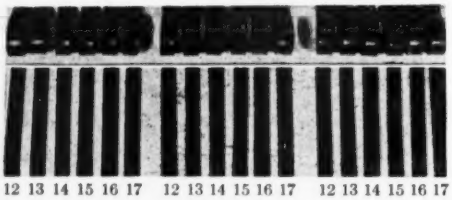

FIG. 8.—Cracking of low-temperature polymer, X-478, after 12 hours' exposure to ultraviolet lamps.

Figures 5 and 6 indicate that the degree of checking was equal for the various types of blacks, regardless of modulus and tensile imparted. Hence it may be assumed that carbon blacks within these varying particle sizes and structures do not affect the rate or degree of checking of vulcanizates when exposed to ozone or weather aging.

Figures 7 through 10 compare vulcanizates containing HAF, EPC, and MAF types of blacks with different types of ozone and sunlight inhibitors. In this comparison there is no significant difference in the effect that the blacks have on either ozone or weather checking. Analyses of the effects of nickel dibutyldithiocarbamate (NBC), a mixture of waxy materials (Heliozone), a *p*-phenetidine derivative (Santoflex AW), and a diphenylamine product (BLE resin), show their sequential rating to be: NBC, best, only slight surface checking; Santoflex AW, second best, mild checking and slight ozone cracking; and Heliozone and BLE, third, best approximately equal for checking and

cracking. It is also noted that the ozone and atmospheric effect is pronounced in these vulcanizates. In Figures 7 and 8, compounds 12, 13, and 14, which contained MAF, HAF, and EPC carbon black, respectively, had 2 parts of NBC added. Compounds 15, 16, and 17 (MAF, HAF, and EPC, respectively) had 1 part of Heliozone added. In Figures 9 and 10, compounds 18 (MAF), 19(HAF), and 20(EPC) contained 2 parts of Santoflex A, while compounds 21(MAF), 22(HAF), and 23(EPC) contained 2 parts of BLE. The six samples on the left in Figures 7 through 10 were cured 40 minutes, the six in the center for 60 minutes, and those on the right for 90 minutes.

The results of ozone exposure on X-478 polymer with no added antioxidant, as shown in Figures 5 and 6, when compared to Figures 7, 8, 9, and 10, which have added antioxidants, suggest that an antioxidant would be desirable and helpful in minimizing the degree of zone and sunlight cracking and checking.

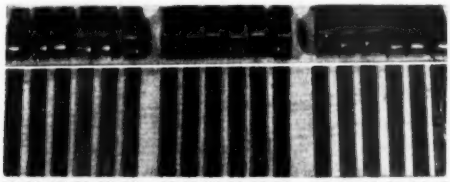

FIG. 9.—Cracking of low-temperature polymer, X-478, after 32 days' exposure to natural sunlight.

Obviously, it is desirable to apply the most reinforcing medium in the sidewall of a tire consistent with economic considerations. The abrasion resistance of MAF black, among numerous other merits, particularly adapts itself to use in this instance; therefore, a MAF black series with recipe variations, developed from the aforementioned observations, was inaugurated.

Figure 11 reflects four MAF vulcanizates which employ the principle of no added antioxidant (exclusive of that used as a polymer stabilizer), reduced sulfur ratio, reduced sulfur ratio with antioxidant added, and reduced sulfur with antioxidant and wax combined in LTP X-478. Respective progressive improvement was observed when the specimens were exposed for 32 days in

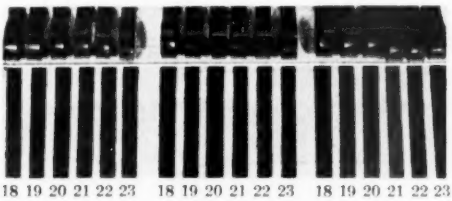

FIG. 10.—Cracking of low-temperature polymer, X-478, after 12 hours' exposure to ultraviolet lamps.

natural sunlight. Figure 12 compares the same vulcanizates as in Figure 11 and the same relative improvement exists when specimens are exposed to 12 hours under the ultraviolet lamp. In both Figures 11 and 12, cure time for the four compounds on the left was 40 minutes, for the four in center 60 minutes,

and for those on the right 90 minutes. In the following table is shown the parts of sulfur, accelerator, and antioxidant added to these vulcanizates.

Compound	7	24	25	26
Accelerator	1.2	1.35	1.35	1.35
Sulfur	1.75	1.4	1.4	1.4
Santoflex AW	—	—	1.5	1.5
Heliozone	—	—	—	1

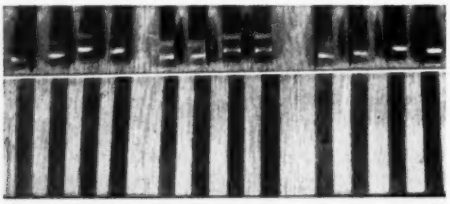

FIG. 11.—Cracking of low-temperature polymer, X-478, after 32 days' exposure to natural sunlight.

Over 400 test-specimens were exposed during this investigation, and the grading comparison was by visual as well as pictorial means. The ratings for specimens shown in Figures 11 and 12, for example, would be as follows:

Cure at 292° F (min.)		Sunlight exposure						Ozone exposure					
		12.5% elongation			180° bend			12.5% elongation			180° bend		
Recipe no.	Rating	40	60	90	40	60	90	40	60	90	40	60	90
7	3	LM	LM	LM	LM	LM	LM	ML	LM	LM	MM	MM	LM
24	3	LM	LM	LM	LM	LM	LM	LL	LL	LL	ML	MM	ML
25	2	LS	LS	LS	SS	SS	SS	ML	MM	MM	MM	MM	SM
26	1	NC	SS	SS	NC	NC	NC	SS	SS	SS	SS	NC	SS

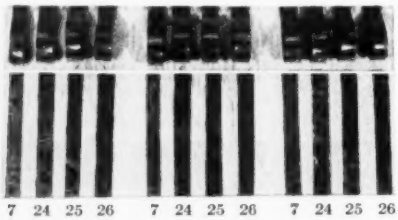

FIG. 12.—Cracking of low-temperature polymer, X-478, after 12 hours' exposure to ultraviolet lamps.

In the above table, the number and depth of checks and (or) cracks in the samples are designated by the same code. Hence, LM signifies a large number of medium depth cracks, LS signifies a large number of small cracks, etc. S = small, M = medium, L = large, and NC = no cracking. The first phase of this investigation pertained to natural-rubber compounds, and the second phase to low-temperature polymer compounds. Although larger amounts of ozone inhibitors were employed in the low-temperature polymer, the natural-rubber compounds resisted ozone better and consequently were exposed for longer periods before cracking became evident. These observations indicate

that natural-rubber compounds resist outdoor and ozone exposure better than low-temperature polymer compounds when tested under static conditions.

CONCLUSION

Carbon black, regardless of type, particle size, structure, and physical properties imparted, does not affect the rate or degree of checking or cracking in natural-rubber or low-temperature polymer compounds when subjected to weather or ozone exposure.

Natural rubber will withstand much longer periods of exposure than the synthetic polymer studied. A pronounced degree of ozone and weather cracking and checking will result if no antioxidant is compounded into the synthetic polymer. An MAF black-synthetic polymer compound may be substantially improved in its resistance to ozone and weather resistance by selection and application of the proper antichecking ingredients.

ACKNOWLEDGMENT

The authors wish to express their appreciation to the Phillips Chemical Co. service laboratory and its personnel for their valuable contribution in preparing and obtaining the data presented in this paper.

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SOME RESULTS OBTAINED IN A STUDY OF THE DEVELOPMENT OF STICKINESS BY VULCANIZED RUBBER *

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INTRODUCTION

When vulcanized rubber is stored by itself, it undergoes spontaneous changes, generally known as aging. The factors which are responsible for these aging effects or which are capable of influencing the progress of aging are many, *e.g.*, oxygen, ozone, light, heat, the nature of the vulcanization accelerator, etc. The general character of the changes resulting from aging may depend on, and vary with, the particular combination of these factors. In general, vulcanized rubber which has aged naturally shows no change in the character of its surface. On the other hand, other aging conditions, which can be regarded as abnormal, are characterized by visible physical changes. These changes in appearance are manifest in two ways:

(1) by a stiffening of the entire mass or of the surface, with ultimate formation of cracks, or

(2) by softening, and the development of an adhesive surface.

This second phenomenon, which is familiar as a form of stickiness so frequently encountered with crude rubber, has not, in the case of vulcanized rubber, been the subject of many scientific investigations. Nevertheless, this type of stickiness often appears during the natural aging of certain vulcanized products, particularly electric cables. The practical and theoretical importance of a study of this phenomenon is, therefore, incontestable. The very infrequent attempts which have been made to reproduce the development of this stickiness have been, in general, unsuccessful.

In the present work we have studied what conditions are necessary for vulcanized rubber to become sticky by aging, as well as the influence of factors inherent to vulcanized rubber mixtures, *e.g.*, compounding ingredients, and finally the influence of external factors, *e.g.*, the aging conditions.

OPERATING TECHNIQUE

In most cases the experiments aimed at the laboratory reproduction of stickiness were carried out under the following three conditions:

(1) in a drawer, *i.e.*, at room temperature and in darkness;

(2) in an unventilated air oven, at temperatures from 60° to 100° C;

(3) in a Bierer-Davis oxygen bomb, at 70° C, and with pressures of oxygen from 1 to 20 kg. per sq. cm.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 29, No. 9, pages 660–663, September 1952. This work was done in connection with technical training at the French Rubber Institute, and the results of the experimentation were presented at the final examination. Because of time limitations, however, the work does not pretend to be complete, but the results seemed of sufficient interest to warrant the present communication.

Since no instrument was available for properly measuring stickiness or softening, reliance had to be put on a contact test, based on the fact that a sticky sample shows a certain degree of adhesion to the finger. In addition, stickiness can be evaluated by estimating the degree of adhesion between two samples. With a certain amount of experience, this method can be conveniently and reliably used to make approximate comparisons, and in particular for the immediate detection of the appearance of stickiness.

To estimate the extent of such degradation, recourse was had to tensile tests, with dumb-bell test-specimens of the French Rubber Institute type. Actually these changes in mechanical properties indicate quite reliably the progress of aging.

INFLUENCE OF FACTORS INHERENT TO VULCANIZED RUBBER MIXTURES

VULCANIZING AGENTS

Based on their effects in aging tests, the particular vulcanizing agents which were examined can be classified in two categories:

(1) those which generally lead to the development of stickiness, among which are benzoyl peroxide and sulfur in the absence of a vulcanization accelerator;

(2) those which do not induce stickiness, among which are trinitrobenzene and tetramethylthiuram disulfide.

VULCANIZATION ACCELERATORS

In order to include a variety of types in the choice of accelerators, both chemical structure and accelerating power were taken into account.

The composition of the mixtures was as follows:

Smoked-sheet rubber	100
Sulfur	3
Stearic acid	1
Zinc oxide	3
Accelerator	1

The accelerators which were examined included thiocarbanilide; diphenylguanidine; mercaptobenzothiazole; an equivalent combination of diphenylguanidine and mercaptobenzothiazole; hexamethylenetetramine; litharge; benzothiazolyl disulfide; butyraldehyde-aniline; tetramethylthiuram disulfide; and zinc ethylphenyldithiocarbamate.

The aging tests in the air oven and in the Bierer-Davis oxygen bomb gave the following results.

The mixtures vulcanized with thiocarbanilide and with diphenylguanidine became sticky, irrespective of the conditions of the accelerated tests.

The mixtures vulcanized with litharge, with hexamethylenetetramine, and with zinc ethylphenyldithiocarbamate became sticky only under certain conditions.

The mixtures vulcanized with mercaptobenzothiazole, benzothiazolyl disulfide, butyraldehyde-aniline, and with the combination of mercaptobenzothiazole and diphenylguanidine showed no evidence of stickiness under any conditions of aging.

There would appear to be some relation between these results and those of

Garvey and Forman (*Ind. Eng. Chem.* **30**, 1036 (1938)) in their study of the effects of accelerators on the phenomenon of reversion.

The results with diphenylguanidine and with mercaptobenzothiazole seemed to be particularly interesting, so a more extensive investigation of these accelerators was made. Figures 1 and 2 show the changes of tensile strength and the oxidizability of the various mixtures.

The curves in Figures 1 and 2 show that the diphenylguanidine vulcanizate, which tended to become sticky, also showed the poorest aging properties and the greatest tendency to oxidize. The first appearance of stickiness was coinci-

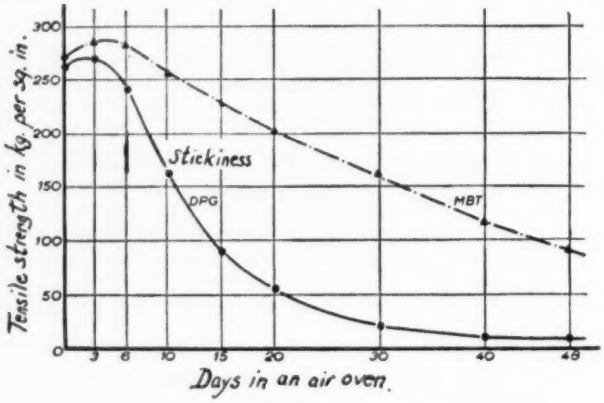

FIG. 1.—Aging in an unventilated air oven at 70° C.

dent with a loss of 37 per cent of its tensile strength. On the contrary, even when the mercaptobenzothiazole vulcanizate had lost 69 per cent of its tensile strength, it showed no appreciable stickiness. Consequently the appearance of stickiness does not necessarily represent an advanced stage of deterioration, but rather merely one particular form of aging.

METAL PROOXYGENIC AGENTS

For a long time it was believed that the presence of prooxygenic metal compounds was necessary for vulcanized rubber to become sticky on aging. This assumption has now been shown to be incorrect, for the present work shows that it is possible to reproduce the development of stickiness in rubber which has been vulcanized with diphenylguanidine or with thiocarbanilide as accelerator and which contains no poisonous compounds of any kind. Nevertheless, it is true that certain iron, manganese, copper, and cobalt compounds do accelerate the appearance of stickiness and intensify its manifestations.

TABLE 1

Mixture	Time for stickiness to appear in an air oven at 70° C	Percentage loss of tensile strength after this time
No copper compound	10 days	37
Copper oleate (0.02% or Cu)	1 day	25

Table 1 shows representative results relating to the influence of a copper compound. Each of the two rubber mixtures was vulcanized with diphenylguanidine.

The order of the different accelerators with respect to the tendency of vulcanizates containing them to become sticky on aging does not change when a prooxygenic metal compound also is present.

STATE OF VULCANIZATION

As is evident from Table 2, undercuring favors the appearance of stickiness on aging. Each of the two rubber mixtures was vulcanized with diphenylguanidine.

TABLE 2

Time of vulcanization (minutes)	Number of days for stickness to appear in an air oven at 70° C	Percentage loss of tensile strength at the time of appearance of stickiness
60 (optimum)	10	37
20 (undercuring)	7	15

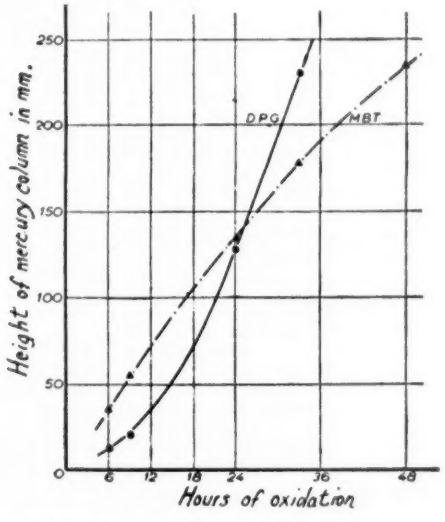

FIG. 2.—Oxidizability measured by a Dufraisse manometer at 80° C.

DEGREE OF PLASTICIZATION OF THE RUBBER

Although excessive mastication was suspected of having a harmful influence, tests showed that it apparently does not have any effect on the appearance of stickiness.

INFLUENCE OF CONDITIONS OF AGING

It is quite evident that the chemical composition of a rubber mixture is not the only factor which governs its behavior on aging, but that the atmosphere plays a dominant role. The influence of five other factors was examined, *viz.*:

pressure of oxygen, sunlight, humidity, confinement of the atmosphere, and the presence of harmful vapors.

TEMPERATURE AND PRESSURE OF OXYGEN

The experiments were carried out with various rubber mixtures, some of which had shown a tendency, others of which had shown no tendency, to become sticky during aging. A more extensive study was made of the rubber mixtures which were vulcanized with diphenylguanidine and with mercaptobenzothiazole.

The experiments on the influence of the pressure of oxygen were made with a Bierer-Davis bomb at 70° C and at pressures of 1, 7, 14, and 21 kg. per sq. cm.

A number of conclusions can be drawn which will aid in explaining the character of the phenomenon of stickiness. The initial manifestation is always a

TABLE 3

Acceleration or vulcanization of the rubber mixture	Original tensile strength (kg. per sq. cm.)	Tensile strength after aging 7 months (kg. per sq. cm.)	Percentage loss of tensile strength after aging 7 months	Percentage loss of tensile strength at the appearance of stickiness in an air oven at 70° C
Vulcanized by diazoaminobenzene	80	12	85	0 to 5
Accelerated by diphenylguanidine (vulcanized 20 min.)	205	117	43	15 to 20
Accelerated by diphenylguanidine (vulcanized 60 min.)	260	92	65	35 to 45
Accelerated by diphenylguanidine (vulcanized 60 min.) and with 0.02% copper	242	49	80	25 to 30
Accelerated by diphenylguanidine (vulcanized 60 min.) and with 0.05% copper	24	35	84	30 to 40

DEGREE OF HUMIDITY

progressive softening, with simultaneous appearance of a marked power of adhesion. After this preliminary stage has been passed, the changes may manifest themselves in two different ways, according to the severity of the aging phenomena.

The first case.—When oxidation progresses slowly (at temperatures below 80° C, and pressures of oxygen less than 7 kg. per sq. cm.), the preceding manifestations are accentuated, and there is progressive liquefaction and the vulcanizate becomes transformed into a kind of viscous or plastic mass.

The second case.—When oxidation proceeds rapidly (at high temperatures and pressures of oxygen), a surface skin or film, which is hard and lustrous, is formed. This varnishlike skin apparently obstructs any further penetration of oxygen, and there is no further deterioration in the interior of the mass. Nevertheless, it should be recognized that the phenomenon of stickiness appears at the beginning of aging, for, during the initial stage of aging, when the vulcanizate softens, it is manifest in characteristic flow and deformation.

SUNLIGHT

Test-specimens which had a particularly strong tendency to become sticky on aging were exposed to sunlight and to outdoor weathering from July to February.

In no case was any tendency to become sticky observed; on the other hand, in every case the test-specimens showed surface hardening. Since, under such conditions, loss of tensile strength is much greater (in fact generally two or three times greater) than that corresponding to the loss when stickiness first appears in an air oven at 70° C (see Table 3), sunlight seems to be a powerful inhibitor of the tendency of a vulcanizate to become sticky on aging.

In the experiments with rubber mixtures which had been vulcanized with diphenylguanidine and with thiocarbanilide, it was found that atmospheric humidity has a marked inhibitory influence on the tendency of the vulcanizates to become sticky on aging In strictly dry air, the tendency of a vulcanizate to become sticky is greatest of all (see Figure 3).

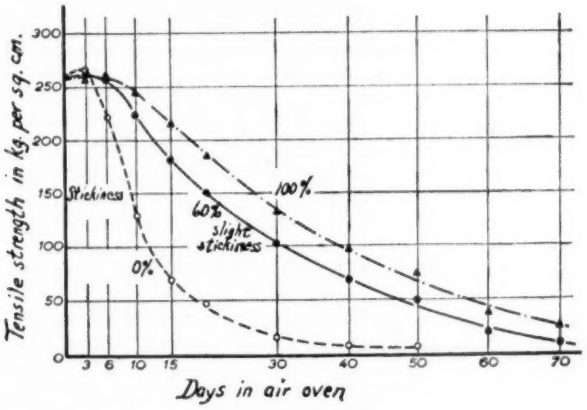

FIG. 3.—Aging of a mixture accelerated by diphenylguanidine in air at 70° C and of different degrees of humidity. Percentage values refer to relative humidity.

Figure 3 shows the aging of a rubber mixture vulcanized with diphenylguanidine in an air oven. In a moist atmosphere, the aging is relatively good. On the other hand, in the case of rubber mixtures vulcanized with mercaptobenzothiazole, the influence of moisture in the air is insignificant.

This effect of humidity can be attributed to the fact that the presence of water vapor reduces the partial pressure of oxygen. In addition, the deposit of water on the surface of the rubber interferes to some degree with contact of oxygen with the rubber. Again, the presence of water plays a direct part in the mechanism of the decomposition of the hydroperoxides, *e.g.*, by a hydrolytic reaction.

CONFINED ATMOSPHERIC CONDITIONS

Confined atmospheric conditions can be defined as those in a closed container of small dimensions, with no ventilation at all. Furthermore, the sample must occupy a major portion of the available volume of the container, so that

any volatile products which are evolved during autoxidation remain at a definite concentration.

It was found that confinement of samples under such conditions does not play any significant part in the rate at which a vulcanizate becomes sticky on aging, but that it does accentuate greatly the visible effects of this aging. An explanation of this must be sought for in the continuous formation of volatile peroxides, which would be eliminated if the system were ventilated.

PRESENCE OF ORGANIC HYDROPEROXIDES

In view of the experimental results which have been described, it seemed of interest to determine the part played by peroxides. The influence of the presence of vapors or decomposition products of cumene hydroperoxide and of *tert*-butyl peroxide in the aging chambers was, therefore, studied. It was found that, under such conditions, the vulcanizates liquefied very rapidly, a phenomenon which is comparable to an extremely rapid onset of stickiness.

SUMMARY AND CONCLUSIONS

The experiments described in the present paper show the possibility of reproducing artificially the stickiness which appears during natural aging, and the results show the experimental conditions which are most favorable to a study of the phenomenon.

The indications are that it is best to use an oxygen bomb of small capacity, at a temperature of 60–70° C, and with a pressure of 1-4 kg. per sq. cm. of oxygen. The factor which under no conditions must be disregarded if almost certain failure is to be avoided is unquestionably the problem of ventilation. The Geer oven does not seem to be of any service in such experimentation.

The appearance of stickiness during aging is not indicative of an advanced stage of deterioration, but is a manifestation of one form or type of aging rather than the consequence of an extreme state of deterioration.

Finally, the influence of certain factors has been established. As far as factors inherent to the rubber mixtures themselves are concerned, the accelerator-vulcanizing agent system plays a determinant part. The character of the phenomenon depends on the aging conditions, particularly on the rate of oxidation. The tendency of a vulcanizate to become sticky on aging is particularly great when the temperature is relatively low and the pressure of oxygen is likewise low.

A CHEMICAL STUDY OF ACCELERATORS OF THE PLASTICIZATION OF RUBBER *

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In the preparation of any kind of rubber mixture, the rubber itself must first be plasticized; in other words, compounding ingredients can be mixed into rubber only when the latter has been made sufficiently soft for powders to penetrate the mass and be dispersed uniformly. This process of mastication preliminary to the mixing operation is very burdensome because of the powerful machinery required and the power consumed.

Substances which have in the past been utilized as plasticizing agents do not have as their principal function the more rapid plasticization of the crude rubber itself, but rather the attainment of better dispersion of the compounding ingredients in the rubber during the mixing operation. However, these agents have grave faults, for, in virtue of their dispersion among the molecules of rubber, they modify the vulcanizing properties of the latter, and they impair the mechanical properties of the final products[1].

TABLE I

COMMERICAL PLASTICIZATION ACCELERATORS

Commercial name	Manufacturer	Composition
R.P.A. no. 1	E. I. du Pont de Nemours & Co.	Complex of phenylhydrazine and zinc chloride $[H_2NNH]_2ZnCl_2$
R.P.A. no. 2	E. I. du Pont de Nemours & Co.	2-Naphthalenethiol (33⅓%) + an inert hydrocarbon (66⅔%)
R.P.A. no. 3	E. I. du Pont de Nemours & Co.	Xylenethiol (36.5%) + an inert hydrocarbon (63.5%)
R.P.A. no. 4	E. I. du Pont de Nemours & Co.	Mixture of aryl thiols
R.P.A. no. 5	E. I. du Pont de Nemours & Co.	Zinc salt of xylenethiol (50%) + a mixture of hydrocarbons (50%)
Peptone-22	Calco Chemical Division of American Cyanamide Co.	*o-o'*-Dibenzamidodiphenyl
Renacit-I*	I. G. Farbenindustrie A.-G.	2-Naphthalenethiol
Renacit-II*	I. G. Farbenindustrie A.-G.	Mixture of trichlorobenzenethiol isomers
Renacit-III*	I. G. Farbenindustrie A.-G.	Anthracenethiol
Renacit-IV*	I. G. Farbenindustrie A.-G.	Zinc salt of pentachlorobenzenethiol
Peptax	Société d'Extraction et de Synthèse Organo-Chimique	Modified phenylhydrazine stearate

* This product is no longer commercially available.

Products which promote the plasticization of crude rubber and reduce the mechanical work necessary, not by dispersion among the macromolecular chains of the rubber but by actually splitting these chains, have been investi-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 29, No. 7, pages 506–510, July 1952. This paper consists of extracts from a work presented at Paris, February 9, 1951, for the granting of the title of Doctor of Engineering.

gated. The plasticizing activity of these agents is of a chemical nature. Furthermore, since the percentages which are necessary for plasticization are very low, the properties of the final vulcanizates are not adversely affected.

Chemical plasticizing agents, which have been available since 1936 under the name of peptizing agents play the part of plasticization accelerators. To the representative list in Table I should be added mercaptobenzothiazole, which is everywhere known as a vulcanization accelerator.

The action of plasticization accelerators in rubber during the process of mastication is too well known to warrant any discussion at this time. We shall confine ourselves to some typical results, and shall describe in particular some experiments which were carried out in an effort to explain the mechanism of this action and some of the important results which have already been summarized in a brief communication[2].

MASTICATION OF RUBBER IN THE PRESENCE OF A PLASTICIZATION ACCELERATOR

COMPARATIVE EXPERIMENTS

Systematic tests were carried out on a laboratory mill for the purpose of comparing the effectiveness of different agents which have been used in the mastication of rubber. The consistency of the mixtures was measured by means of the Mooney viscometer after increasing times of milling.

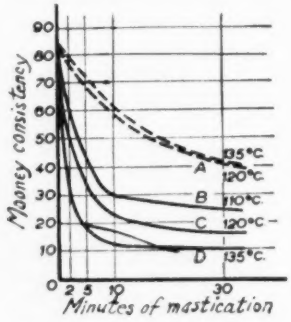

Fig. 1.—Mastication in the presence of 2-naphthalenethiol.

A no addition
B 0.2% 2-naphthalenethiol
C 0.2% 2-naphthalenethiol
D 0.2% 2-naphthalenethiol

Figures 1 and 2 record some results obtained with 2-naphthalenethiol and with mercaptobenzothiazole and two derivatives of the latter. These experiments show the importance of operating at elevated temperatures.

The most effective agents belong to the class of aromatic thiols, such as 2-naphthalenethiol and xylenethiol.

Mercaptobenzothiazole is a less powerful plasticization accelerator than is 2-naphthalenethiol. Although the former gives very plastic mixtures when mastication is carried out at elevated temperatures, this effect is slow to develop. On the contrary, 2-naphthalenethiol acts very rapidly, and this same distinction is encountered in actual practice.

The zinc salt of 2-naphthalenethiol is less effective than 2-naphthalenethiol

itself, and naphthyldithionaphthalene has no plasticizing power at all. Likewise, the zinc salt of mercaptobenzothiazole and benzothiazolyl disulfide are less effective than is mercaptobenzothiazole.

Tertiary aliphatic thiols, phenylbenzothiazole, mercaptothiazoline, and mercaptobenzimidazole were found to be without plasticizing power, whereas diphenylthiocarbazone was very effective.

MODIFICATION OF THE EFFECT OF PLASTICIZATION ACCELERATORS

When plasticization accelerators are added to rubber at the beginning of the milling operation, they act on the rubber in the absence of any accessory agent. When certain other ingredients are added, the effectiveness of the accelerators is changed completely. This is of great practical importance when the disturbing agents are ingredients normally used in rubber mixtures. For example, in the presence of traces of sulfur, selenium, or tellurium, the effectiveness of a plasticization accelerator is completely inhibited, and plasticization progresses as if no accelerator were present.

This inhibitory effect of sulfur and of metalloids of the same group cannot be explained by a simple chemical reaction between sulfur and the thiol, for a ratio of one atom of sulfur to twenty molecules of 2-naphthalenethiol is sufficient to bring about total inhibition of the accelerating effect on plasticization. Some action of a catalytic nature must, therefore, be assumed. A spectrographic examination, which will be described later, of the reaction serves to explain the phenomenon.

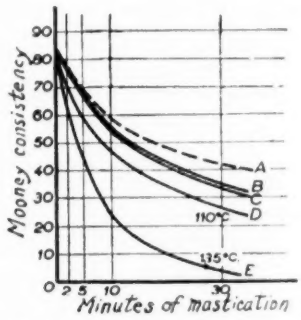

FIG. 2.—Mastication in the presence of mercaptobenzothiazole and some of its derivatives.

A No ingredient
B 1% benzothiazolyl disulfide
C 1% zinc salt of mercaptobenzothiazole
D 1% mercaptobenzothiazole
E 1% mercaptobenzothiazole

The only effect of zinc oxide is to retard the plasticizing action. Phenyl-β-naphthylamine has a slight retarding action on plasticization in the presence of 2-naphthalenethiol, and dibutylamine and stearylamine have pronounced retarding effects. On the other hand, mercaptobenzimidazole has no appreciable influence.

These experiments show that certain precautions are necessary when plasticization accelerators are employed; the rubber must be masticated with only the plasticization accelerator present until the desired plasticity is attained. In turn, when the desired plasticity is reached, the addition of sulfur

prevents the mixture becoming too plastic and tacky by nullifiying the action of the plasticizing accelerator.

ACTION OF PLASTICIZATION ACCELERATORS ON RUBBER SOLUTIONS

The term peptizing agent, which was first proposed for these accelerators, probably originates from their effect on the viscosity of rubber solutions, which can be shown by the following experiment.

Place 1 gram of finely cut rubber sample and a plasticization accelerator in a test-tube of 70 cc. capacity, add 50 cc. of xylene, close the tube, allow to stand in darkness for 24 hours, heat in boiling water for the desired length of time, (protecting from light), and finally measure the viscosity of the solution at room temperature by the time of descent of a ball between two reference marks on a calibrated tube placed at an angle of 30° to the vertical. The viscosity is

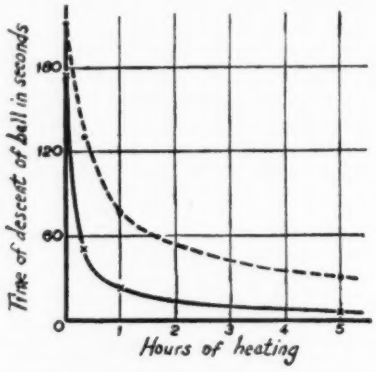

FIG. 3.—Viscosity as a function of the time of heating. Solid curve—1% 2-naphthalenethiol; Broken curve—no added ingredient.

proportional to the time of descent of the ball. Figures 3 and 4 show the influence of the proportion of 2-naphthalenethiol and of the time of heating of the solutions at 100° C.

Heating a solution of rubber in xylene at 100° C reduces its viscosity, and the longer the time of heating, the greater is the reduction. If the solution contains 2-naphthalenethiol, the lowering of the viscosity by the heating is greater than it is for a corresponding solution containing no 2-naphthalenethiol. Moreover, even at room temperature, this agent lowers the viscosity of rubber solutions, provided that it is present in high enough proportions, *i.e.*, 5 per cent of the weight of the rubber. In contrast to this, 0.5 per cent is sufficient when the solution is heated for one hour at 100° C.

A comparison of the viscosities of solutions prepared in open air and in a vacuum shows the influence of oxygen on the viscosity, a phenomenon previously studied by Kheraskova and Gamayunova by a different method[3].

Tubes containing 1 gram of rubber and different proportions of 2-naphthalenethiol were connected to a mercury pump to obtain a vacuum of 2×10^{-2} mm. of mercury, and then to a flask containing xylene which had previously been degassed. After adding 50 cc. of xylene, the tubes were sealed, and the sealed tubes were heated for one hour in boiling water, were cooled to room temperature, were then opened, and the viscosities were measured immediately.

The results of these measurements, compared to those obtained with the corresponding solutions prepared in open air, are shown Table II.

TABLE II

TIME OF DESCENT OF BALL IN SECONDS

	Solution heated	
	In a vacuum	In open air
No ingredient	182	78
2-Naphthalenethiol (0.5%)	212	27
2-Naphthalenethiol (5%)	160	20

Two facts are established by these experiments:

(1) Heating a solution of rubber containing no other ingredients and prepared in a vacuum does not reduce its viscosity, in contrast to the effect of heating a corresponding solution prepared in open air.

(2) The addition of 2-naphthalenethiol does not reduce the viscosity of a solution of rubber prepared in a vacuum and then heated.

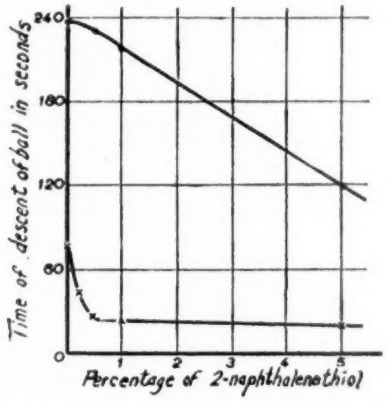

FIG. 4.—Viscosity as a function of the concentration of 2-naphthalenethiol. Upper curve—Unheated solution; Lower curve—Solution heated 1 hour at 100° C.

In brief, measurements of the viscosities of solutions show on the one hand that atmospheric oxygen is responsible for the lowering of the viscosity of these solutions and, on the other hand, that this lowering of the viscosity is promoted by heating in the presence of 2-naphthalenethiol.

MECHANISM OF PLASTICIZATION BY THIOLS

It has just been shown that certain aromatic thiols play the part of plasticization accelerators. By a study of their influence on the oxidizability of rubber and their transformations during the reaction, it becomes possible to explain the mechanism of their action.

OXIDIZABILITY OF RUBBER IN THE PRESENCE OF A PLASTICIZATION ACCELERATOR

The part played by oxygen in the plasticization of rubber is well known[4].

Small amounts of oxygen promote the formation of peroxides, which in turn bring about scission of the macromolecular chains, *i.e.*, plasticization.

In the work described in the present paper, the oxidizability of rubber in the presence of different plasticization accelerators was studied with the aid of a manometer already used for measuring oxidizability[5].

The technique was to disperse the plasticization accelerator in one gram of rubber sample by a few passes on a cold micromixing mill, then to roll up the mixture, in the form of a thin ribbon, in a piece of filter paper, and place the roll in the manometer at 80° C.

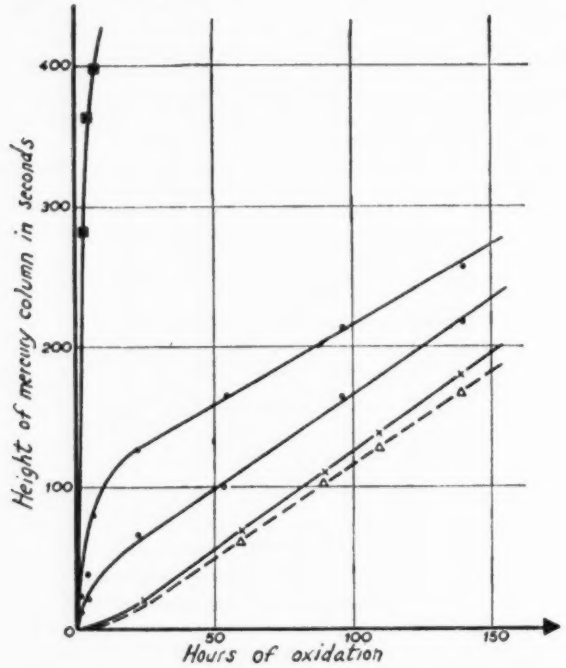

FIG. 5.—Oxidizability of rubber in the presence of 2-naphthalenethiol.

■ 5%
● 1%
○ 0.5%
+ 0.2%
△ no addition

Oxidation of the rubber containing 2-naphthalenethiol was very rapid at first, and the higher the initial proportion of 2-naphthalenethiol, the more rapid and intense was the oxidation (see Figure 5).

After several hours in oxygen at 80° C, the curves in Figure 5 become parallel, and the rates of oxidation become the same.

Judged by the shape of the curves in Figure 5, oxidation involves two phases. Rapid absorption of oxygen at the beginning is the result of a catalytic action of the thiol. Subsequently, oxidation of the rubber progresses normally as it would if the influence of the catalyst were no longer appreciable.

With mercaptobenzothiazole, the course of the curves is less characteristic,

and transition from the first to the second phase of oxidation is a progressive one (see Figure 6).

The zinc salt of mercaptobenzothiazole has less influence on the absorption of oxygen by rubber, and benzothiazolyl disulfide has only a very weak catalytic action. In general, the order of activity of these products with respect to their effects on the oxidation of rubber is the same as that of their effects on plasticization.

Sulfur retards the oxidation of rubber in the presence of mercaptobenzothiazole (see Figure 6) in the same way that it inhibits the action of mercaptobenzothiazole during mastication.

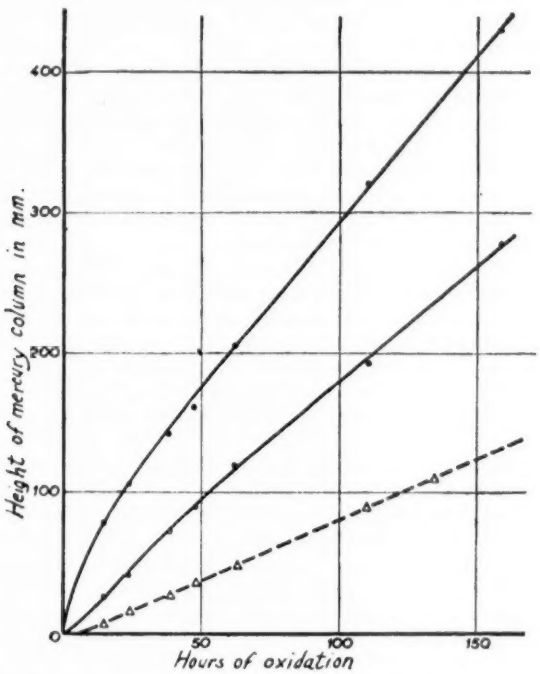

FIG. 6.—Oxidizability of rubber in the presence of mercaptobenzothiazole.

● 1+ Mercaptobenzothiazole
○ 1% Mercaptobenzothiazole + 1% sulfur
△ No added ingredient

Diphenylthiocarbazone, nitroso-β-naphthol, and benzoyl peroxide, all of which promote the plasticization of rubber, likewise accelerate its oxidation.

This phenomenon is, therefore, a general one, and is not limited to thiols. Substances which activate plasticization increase the sensitivity of rubber to oxygen.

STUDY OF THE TRANSFORMATION OF THIOLS

The absorption of oxygen by rubber in the presence of a plasticization accelerator takes place in two phases, and this fact would lead one to believe that

the thiol, which accelerates this oxidation, is transformed into an active form.

Because of the very small amount of product to analyze, ultraviolet absorption spectrography was the indicated method for studying this transformation. This method had already been applied to the analysis of the transformations which some vulcanization accelerators undergo.

We shall not describe the details of the operating technique, because they have been reported in earlier publications[6]. Isolation of the thiol or its transformation products from within the rubber is difficult, and the simplest way to avoid this trouble is to extract the reaction products with acetone in a Soxhlet apparatus. However, the acetone extract of rubber contains, not only the products which are concerned in the present problem, but numerous other substances which are improperly termed resins and the spectra of which are superposed on those of the thiol.

Attempts to separate these substances chromatographically in an alumina column did not give any quantitative results.

In addition, experiments were carried out with crepe rubber which had been purified by extraction with acetone. The purified crepe was mixed on a hot mill with the thiol. The latter and its transformation products were then isolated from the rubber by a new extraction with acetone. After evaporation of the acetone, the extract was taken up in a definite volume of chloroform, and the spectrum of the solution was obtained.

When purified crepe was mixed with 0.5 per cent of 2-naphthalenethiol, the latter was transformed from the start of the mixing operation into naphthyldithionaphthalene, and finally completely into the latter.

In the presence of 0.5 per cent of mercaptobenzothiazole, the spectrum of the latter changed to that of benzothiazolyl disulfide only after 15 minutes' milling at 100° C; however, although this transformation was slower than that of 2-naphthalenethiol, formation of benzothiazolyl disulfide was finally complete.

The inhibiting action of sulfur, already observed in the plasticization and oxidizability experiments, was studied further. Crepe was milled with 0.5 per cent of mercaptobenzothiazole and 0.1 per cent of sulfur at 100° C, and, in another experiment at 120° C with 0.02 per cent of sulfur alone. In neither case after 20 minutes of milling was there any appreciable transformation of mercaptobenzothiazole into benzothiazolyl disulfide.

Transformation of thiol into disulfide in rubber was found to be a function, not of the time of milling, but of the time of storage of the rubber mixture in oxygen.

The results of the spectrographic method confirm the view of Twiss[7] that mercaptobenzothiazole is transformed into benzothiazolyl disulfide during hot milling, and they show also that 2-naphthalenethiol is transformed into the corresponding disulfide.

CONCLUSIONS

Based on the results of the experiments described in the present paper, it would seem still premature to suggest any general mechanism for the action of plasticization accelerators. It has been shown merely that there is a definite relation between these experiments and those of Farmer, according to which oxygen fixes on rubber, with formation of hydroperoxides, the decomposition of which in turn brings about scission of the macromolecular chains.

The experiments also demonstrate a close correlation between the absorp-

tion of oxygen by rubber and plasticization of the latter. This is good proof of the purely chemical character of this latter effect, which is catalyzed only by plasticization accelerators, which sensitize rubber toward oxygen and promote oxidative scission of the macromolecular chains.

With respect to the action of thiols, the following theory may be advanced. The presence of a definite quantity of thiol causes rapid absorption by rubber of a correspondingly definite quantity of oxygen. This accelerated oxidation is, however, only fugitive, for simultaneously the thiol is transformed into the corresponding disulfide, and the sensitizing action ceases as soon as the thiol has undergone this transformation.

The similarity of structure of these agents and of deactivating agents[8] should be noted. From the practical point of view, a result of this similarity is that a rubber mixture which has been plasticized in the presence of 2 naphthalene thiol shows better aging properties than a corresponding mixture which has been plasticized by simple milling. In the same way, a rubber mixture containing 2-naphthalenethiol and phenyl-β-naphthylamine ages better than a corresponding rubber mixture protected only by phenyl-β-naphthylamine. This is a particularly favorable effect.

The complex nature of the chemistry of rubber is evident when one considers the varied roles played by certain aromatic thiols. Mercaptobenzothiazole is a plasticization accelerator for crude rubber, a vulcanization accelerator when sulfur is present, and its zinc salt is a deactivating agent for peroxides. This means, therefore, that a single compound promotes the oxidative scission of macromolecular chains and also is instrumental in the formation of intermolecular sulfur bridges and in the orientation of peroxides in vulcanized rubber.

SUMMARY

Substances which peptize rubber, of which the most active fall within the class of aromatic thiols such as 2-naphthalenethiol and xylenethiol, are also accelerators of plasticization. Their action, which differs from that of "plasticizers", is of a chemical nature, and it can be modified by certain agents, such as metalloids of the sulfur family. The use of plasticization accelerators requires certain precautions.

A study of the oxidizability of rubber in the presence of plasticization accelerators has shown that these substances make rubber more sensitive to oxygen, whose part in the plasticization of rubber is already well known. At the beginning of the reaction, oxygen is absorbed rapidly under the catalytic influence of the thiol, which is simultaneously transformed into the corresponding disulfide.

By means of ultraviolet spectrography, this transformation of thiols while playing the part of catalytic agents can be followed.

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THE EFFECT OF SOFTENERS IN RUBBER *

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The use of oils and liquid softeners to assist in the mastication and processing of rubber or to produce softer vulcanized stocks has been standard practice since the early commercial use of rubber. More recently certain synthetic rubbers, polymerized under special conditions, have been treated with rather large amounts of mineral oils, with a resulting decrease in the cost of the rubber and apparently with no unfavorable effect on the rubber in most instances.

A number of investigators have reported the effect of swelling agents on the properties of vulcanized rubber. Busse[1] discusses the effect of solvents in a general way. Tiltman and Porritt[2] conclude that the decrease in modulus caused by swelling in benzene is caused by a "loosening of cohesive forces." Tire treads of natural rubber containing such softeners as pine tar and mineral rubber decrease in wear resistance in proportion to the softener content[3]. Well vulcanized rubber of high modulus is most resistant to swelling in oils[4]. Naunton, Jones, and Smith[5] find that unaccelerated stocks lose the most tensile strength after being swollen, that milling of the raw rubber increases swelling, and that the presence of softeners in the rubber during vulcanization reduces the oil resistance. A limited amount of swelling has been reported to have little effect on the tensile strength of vulcanized natural rubber[6]. Bourbon[7] points out that separating the rubber molecules with solvent decreases the rate of vulcanization.

Softeners could have a decidedly different effect on vulcanized rubber, depending on the manner of introduction. If the softener is present during vulcanization, the rubber would be vulcanized while in a swollen condition and the manner and degree of bonding into a vulcanized network could be affected. Softeners would also act as solvents for the vulcanizing agents and decrease their effect concentration. Softeners added after vulcanization could not affect the vulcanization process, but would produce a vulcanizate in a condition of strain.

It is possible to produce two sets of vulcanized rubber of the same composition by two different routes. The first set can be obtained by vulcanizing one compound without softener and a second compound with softener, followed by extraction of the softener after vulcanization. The second set can be obtained by vulcanizing one compound in the presence of softener and a second in the absence of softener, followed by diffusion of the softener into the vulcanized rubber. This gives one set without softener and one set containing softener, and in each set one compound is vulcanized in the presence of softener and the other in its absence.

Natural-rubber compounds prepared under the conditions just described consisted of 100 parts of smoked sheet, 5 parts of zinc oxide, 3 parts of sulfur,

* An original contribution. The paper is substantially the same as a paper entitled "The Effects of Oils in Rubber," which was presented by the author at the 60th Meeting of the Division of Rubber Chemistry of the American Chemical Society, at Cincinnati, April 30–May 2, 1952. For information on "Some Effects of Solid Fillers in Rubber," see the following paper, by the same author, in this issue of RUBBER CHEMISTRY AND TECHNOLOGY.

and one part of diphenylguanidine, to which was added 25 parts of Circo light oil, a mineral oil. The two compounds necessary for preparing the two sets were each vulcanized at 287° F. Dumbbell test-strips were cut from the unsoftened stock and were gauged for thickness before being swollen. This assured that the same amount of rubber was present in the unsoftened and swollen stocks. The softener was painted evenly on the surface of the dumbbell and allowed to diffuse into the rubber. This method prevents the excessive diffusion of one component of the softener which might result if the rubber was immersed in an excess of a mixed hydrocarbon. In a similar manner, dumbbell strips were cut from the softened stock and gauged before being acetone-extracted to assure a comparison of the same amounts of rubber. Since the softened compounds contained only 81.5 per cent as much rubber by volume as the unsoftened, all figures obtained with the stocks vulcanized with the softener were divided by 0.815 in order to enable a comparison based on the same volumes of rubber in all four compounds. The results of these test are shown in Table I.

TABLE I

Min. cure	Lbs. per sq. inch at elongation of 400%	500%	600%	Tensile strength (lbs./sq. in.)	% Elongation
		Vulcanized without oil			
30	360	600	1210	2980	750
45	390	700	1525	3400	730
60	460	810	1840	3600	720
		Oil diffused in			
30	325	560	1150	2900	755
45	380	760	1600	3000	690
60	475	910	1800	2950	700
		Vulcanized with oil			
30	221	306	515	2670	840
45	257	416	735	2780	820
60	306	460	865	2650	740
		Oil extracted			
30	233	318	552	2330	800
45	276	429	795	2700	795
60	294	478	877	2450	750

The results show that the compound vulcanized in the presence of oil is soft and remains soft even after the oil has been removed. On the other hand the rubber vulcanized in the absence of oil has higher modulus and retains its stiffness even after oil has been diffused into the compound. This indicates that the relatively small amount of inert softener which was employed is sufficient to interfere with the bonding of the rubber units into a well vulcanized network, but once the network is formed the introduction of softener does not destroy it. While the tensile strength of the rubber was only slightly reduced, it cannot be assumed that larger amounts of softener will not produce a greater reduction or that all softeners will give quantitatively the same results. Softeners usually produce a considerable reduction in tensile of rubbers less organized than natural rubber[8].

Experiments similar to the above can be conducted with other softeners such as pine oil, decanol, or other liquids which do not affect vulcanization, with substantially the same results.

Neoprene is an example of a moderately organized rubber of a highly polar

nature, and in this case the vulcanization step is carried out without sulfur so that a different type of bonding into a vulcanized network is obtained. A compound was prepared from 100 parts of Neoprene Type GN, 5 parts of zinc oxide, 4 parts of magnesia, 1 part of stearic acid, and 0.5 part of 2-mercpato-imidazoline. To this base compound 25 parts of diphenyl ether was added as softener in the same manner as that employed with natural rubber. The com-

TABLE II

EFFECT OF SOFTENER IN NEOPRENE TYPE GN

Lbs. per sq. in. at elongation of				Tensile strength	% Elongation
200%	300%	400%	500%		
Vulcanized without softener					
230	355	540	930	2700	630
Softener diffused in					
195	320			360	330
Vulcanized with softener					
90	130	210	335	390	520
Softener extracted					
80	125	190	330	740	630

pound was vulcanized for 30 minutes at 300° F. The results of tests, based on equal quantaties of rubber, are shown in Table II.

In the case of Neoprene, the effect of softener on the modulus is similar to the effect with natural rubber. However, the diffusion of diphenyl ether into the vulcanized Neoprene resulted in low elongation at break and low tensile. Diphenyl ether has a greater effect in this respect than less polar softeners such as aromatic mineral oils.

Unorganized rubbers such as butadiene-styrene polymers are affected in the same manner as natural rubber or Neoprene by the presence of softeners. For the study of GR-S types of rubber, three mixtures were vulcanized, the third one containing increased amounts of vulcanizing agents in proportion to the amount of softener added. The compounds shown in Table III were vulcanized at 300° F, and the resulting data are shown in Table IV. All data are

TABLE III

BUTADIENE–STYRENE RUBBER COMPOUNDS

	A	B	C
L.T.P.	100.	100.	100.
H.A.F. carbon black	40.	40.	40.
Zinc oxide	5.	5.	5.
Sulfur	1.8	1.8	2.25
Santocure	1.	1.	1.25
Stearic acid	1.5	1.5	1.875
Circo light oil	0.	25.	25.

calculated to the same volume of rubber as that contained in the unsoftened compound.

The bonding of rubber into a vulcanized network requires that the active points be positioned correctly relative to one another. Rubber approaches a solid state and lacks the mobility necessary to reposition reactive points to any great degree. The above data indicate that a small amount of swelling can

separate points at which bonding might occur without proportionally increasing the mobility so that a decrease in the extent of vulcanization results.

Inert softeners such as mineral oils appear to have an unfavorable influence as far as producing high modulus and tensile and probably good abrasion is concerned, and their extensive use could be questioned. However, butadiene-styrene polymers have been produced in the past under conditions which form considerable low molecular-weight and nonrubber material which remains in the product as a softener. Elimination of this material and replacing it with

TABLE IV

EFFECT OF SOFTENERS ON L.T.P. COMPOUNDS

Min. cure	Lbs. per sq. inch at elongation of 200%	300%	400%	Tensile strength	% elongation
		Compound A			
45	760	1700	2820	3480	460
60	940	2000	3140	3560	430
		Compound A with softener diffused in			
45	820	1720		1720	300
60	960	2020		2020	300
		Compound B			
45	238	619	1240	2640	605
60	310	785	1450	2950	590
		Compound B extracted			
45	250	650	1200	3120	650
60	300	750	1350	2780	560
		Compound C			
45	452	1215	2200	2970	460
60	547	1360	2450	2760	420
		Compound C extracted			
45	480	1160	2120	2920	470
60	520	1300	2350	2620	420

and oil, without altering the nature of the rubber polymer, should not materially alter the properties, and would provide a reduction in the cost. If the nonrubber polymers could be eliminated without increasing the average molecular weight of the rubber to a point where it is dry and resists swelling, the oil extended rubber could even be superior. It follows that polymerization to produce intermediate polymers, neither too low to be rubber nor so high as to be dry, insoluble, and too hard to conform to the surface of pigments, should produce material superior to oil-extended rubbers.

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[8] An *organized rubber* is one which develops good physical properties when vulcanized in the absence of substantial proportions of finely divided solid fillers. An unorganized rubber requires the presence of such fillers.

SOME EFFECTS OF SOLID FILLERS IN RUBBERS *

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The presence of pigments in rubber compounds produces physical properties which are of importance both before and after vulcanization. The ability of the unvulcanized mixture to calender or extrude smoothly with minimum swelling and to maintain shape during air cures, and the tensile strength, tear resistence, and abrasion resistance of vulcanized stocks all are affected. The methods by which these changes are brought about have been considered by many investigators and have been summarized by Parkinson[1] and by Shepard, Street, and Park[2]. Since carbon black is the most generally useful reinforcing pigment, it is natural that investigations have been directed particularly to this product. However, while it is recognized that differences exist in the final properties imparted by different pigments, all solid compounding ingredients have something in common. This point can be illustrated by the tear resistance imparted by such a variety of pigments as carbon black, zinc oxide, whiting, and clay. The effect of volume loading on the tear resistance of vulcanized stocks containing these materials, determined by the method of Zimmerman[3] is shown in Figure 1.

The effect of solid compounding ingredients can be studied only by considering the compound as a whole, since the properties are determined very largely by the relation between the solid particle and the matrix which surrounds it. Since the introduction of the many types of synthetic rubbers, the complexity of the problem has been greatly increased by the different states of polymerization, which affect the ability of the rubber to conform to the shape of the pigment particle and by the differences in polar nature which affect the type and the degree of adhesion between filler and matrix.

The nature of the problem can be understood by a consideration of the general rubber compound shown in Table 1. The rubber compound is shown to be composed of three main parts. The chemicals, however, are shown only because of their known importance and will not be considered further because they are to a large extent soluble and become part of the matrix.

The type of matrix is of importance for several reasons. Pigment distribution depends to a considerable extent on the adhesion between the matrix and the pigment. When the matrix is polyphase, the pigments tend to accumulate in the more mobile phase. Chemicals also tend to distribute between the different phases in an unequal manner, depending on the solubility of the chemical in each phase. The final vulcanized phases have different characteristics and produce unequal distribution of stress. If adhesion is insufficient between the phases, a dispersed phase functions much as a filler. For the purpose of studying the action of pigments it is, then, undesirable to employ a matrix of more than a single phase.

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Fillers can be divided into wet and dry types. Wet types are those which show a high degree of adhesion to rubber. It follows that no sharp line of division can exist, because all degrees of adhesion may be found, ranging from very high with carbon black and natural rubber to very low with this rubber and kaolin. The classification also depends on the type of matrix employed. Kaolin, for example, which is a typically dry pigment in natural rubber, is a highly wet pigment in Neoprene. Certain pigments, of which carbon black is one, tend to be wet in either a polar or a nonpolar matrix.

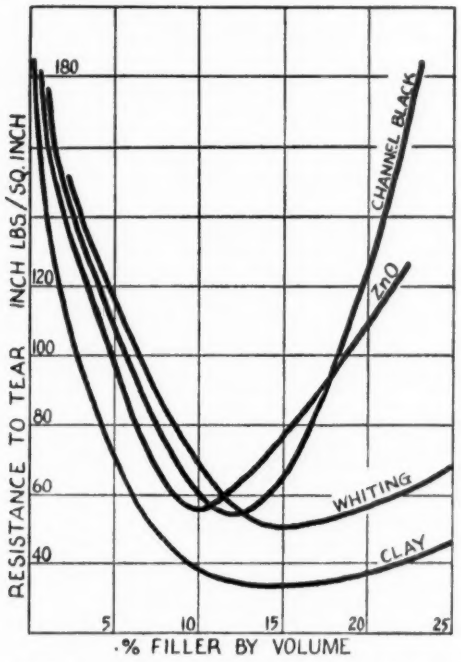

FIG. 1.—The effect of various pigments on the tear resistance of rubber vulcanizates.

EFFECT OF PARTICLE SIZE AND SHAPE

Much has been written about the effect of the shape[4] of the dispersed particle on the properties of the compound, but usually without consideration of the type of matrix. Consider the typically dry pigment kaolin suspended in natural rubber which is flowing under shear, such as that produced by mastication. The ratio of length to thickness of a platelet of kaolin is roughly ten to one. If the plate of kaolin cuts the maximum number of planes of flow, it will tend to rotate because of the relative difference in rate of flow at the two ends of the kaolin plate. Rotation continues at a decreasing rate until the plate lies in the plane of shear, where it tends to remain, because the difference in the rates of flow of the rubber at the two surfaces of the platelet of kaolin is at a minimum. Since the rubber does not wet the plate, the drag on the surface is not always sufficient added force to continue the rotation, and a decided grain

effect is produced in the compound. On the other hand a matrix, such as Neoprene, which wets the surface produces continued rotation of the particle, and the effect of particle shape becomes much less important.

Crowding of pigments leads to resistance to flow and flocculation. In order that flow may take place without interference, each particle of pigment should lie within a sphere of rubber, the diameter of which is equal to the greatest dimension of the pigment. It is obvious that spherical pigments should require the least rubber for the mixture to flow without interference between particles of pigment, but crowding of spherical pigments, even of wet types, leads to flocculation.

For simplicity, consider a brick shaped particle which for free rotation in the matrix requires a sphere of rubber, the diameter of which is equal to the diag-

TABLE 1

GENERAL RUBBER COMPOUND

Matrix			Filler (In natural rubber)	
Single phase	Polyphase	Chemicals	Wet	Dry
Natural rubber	Many mixed rubbers such as natural + Neoprene or nitrile types	Sulfur	Carbon	Kaolin
Most synthetic rubbers	Rubber + factice	Accelerators	Zinc oxide	Whiting
Rubber and many oils or tars	Rubber + reclaim	Antioxidants	Zinc sulfide	Calcium silicate
Natural rubber and low molecular-weight GR-S types	Rubber + many oils and waxes such as castor oil or shellac	Activators	Red oxide (These tend to be hydrophobic)	(These tend to be hydrophylic)
	Probably some highly polymerized synthetic rubbers	Plasticizers, etc.		

onal of the brick. Now cut the brick once in each direction to produce eight smaller bricks of the same relative dimensions as the original. The eight smaller spheres of rubber exactly equal the volume of the single large one and nothing has been accomplished except to double the surface area. Now cut the brick only once across the long dimension to produce two pieces which have decreased length in proportion to the other dimensions. The volume of the two spheres of revolution is now only 0.56 of the original single sphere, and the pigment has approached sufficiently close to a spherical shape to be considered as such for all practical purposes. The decreased resistance to flow of kaolin suspended in water caused by change in the relative dimensions has been confirmed by the work of Millman[5].

The effect of particle size on a single type of pigment under wet and dry conditions can be well illustrated by means of kaolin fractionated to produce pigments of different size and mixed into both natural rubber and Neoprene. Each rubber was compounded with a 35-volume loading of each pigment, and the load at a fixed elongation, tensile strength, and tear resistance was determined. The tear resistance was measured with Goodrich crescent test-pieces. Electron micrographs of the two samples of kaolin are shown in Figures 2 and 3, and the results are shown in Table 2.

It is apparent that fine particles are of importance when the pigment is

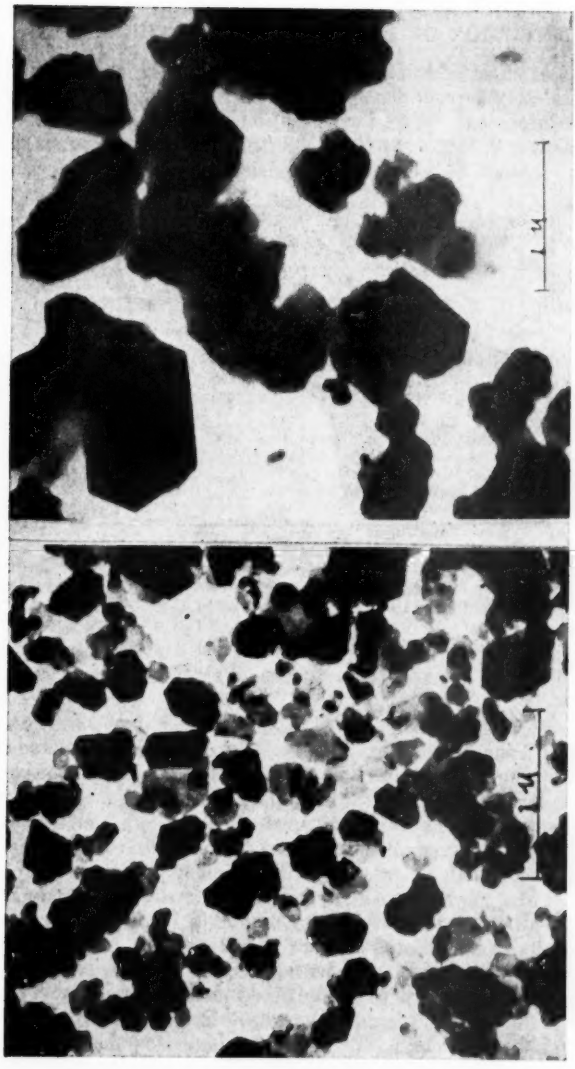

FIG. 2.—Electron micrograph of fine kaolin.

FIG. 3.—Electron micrograph of coarse kaolin.

wetted by the matrix, but are of much less importance when it is dry. It is also apparent that spherical pigments are not necessary to produce reinforcement. Fine kaolin in Neoprene produces a tear resistance which approaches that produced by carbon black.

DISTRIBUTION OF PIGMENTS WITHIN THE MATRIX

If the greatest effect of the pigment is assumed to be produced when each particle is completely surrounded by rubber, then the distribution of the particles becomes important. The incorporation of pigments with any type of mixing equipment is at first mechanical, and consists in trapping small portions in folds of the rubber. Subsequent dispersion depends on the tendency of the

TABLE 2

EFFECT OF PARTICLE SIZE

Cure (min.)	400% Modulus (lb. per sq. in.)	Tensile strength (lb. per sq. in.)	Tear resistance (lbs./in.)
	Smoked Sheet—Coarse kaolin		
30	1830	2890	170
60	1945	3070	158
75	1960	2990	168
	Smoked Sheet—Fine kaolin		
30	1890	2900	160
60	1935	2900	174
75	1975	3000	170
	Neoprene—Coarse kaolin		
30	1100	1860	268
60	1170	1870	274
75	1190	1800	292
	Neoprene—Fine kaolin		
30	1680	2160	468
60	1840	2250	431
75	1940	2250	440

pigment to form coherent clusters, on the degree of adhesion between matrix and solid, and on the degree of crowding. Kaolin, for example, does not readily form coherent clusters and disperses well, particularly in a matrix such as Neoprene, which wets the particle. All types of carbon are wet by rubber, but most fine carbons form more cohesive clusters than coarse carbons and are more difficult to disperse. In any case good dispersion requires sufficient matrix to provide flow of the mixture without excessive interference between pigment particles. Crowding, particularly of dry pigments, leads to excessive flocculation, but typically wet pigments also are flocculated.

If a pigment consisting of uniform spheres is considered, the theoretical space relationship of the particles can be determined. Spheres can be arranged in a number of different patterns, but the minimum amount of voids is produced by rhombohedral packing in which 12 spheres touch every other sphere, and the voids constitute 26 per cent, and the pigment 74 per cent of the volume. It is possible to conceive of the same number of smaller spheres being distributed in such a manner that their center occupies the same position as the spheres in rhombohedral packing; the space between is taken up by matrix. The distance between particles of pigment and the thickness of the film of matrix

can then be calculated in terms of the diameter of the dispersed spheres. This type of packing gives the greatest distance between spheres, and any deviation means that the spheres approach more closely at some points. The distance between particles in rhombohedral spacing for various volumes of pigment is shown in Figure 4, in which the unit of measurement of the distance between

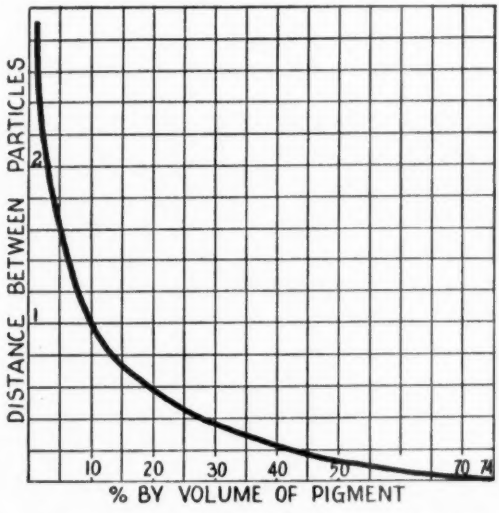

FIG. 4.—Assuming that each particle is at the center of spheres arranged in rhombohedral packing, this curve shows the distance between the surfaces of the particles in terms of the diameter of the particles.

the particles is the diameter of one of the dispersed spheres. It is quite evident that, with ideal dispersion, the particles of pigment in such a compound as a tire tread are scarcely farther apart than the diameter of the pigment, as demonstrated below.

The space relation between particles in a tire tread under conditions of ideal dispersion can be determined as follows:

Matrix	Lbs.	Volume	Pigment	Lbs.	Volume
Rubber	100	108.7	Zinc oxide	5	0.9
Stearic acid	3	3.5	Black	50	26.3
Oils	5	5.9			
Chemicals	2	1.6			
Sulfur	3	1.5			
Total	113	121.2		55	27.2
% by volume		81.7			18

Reference to Figure 4 shows that the distance between particles in a compound containing 18.3 per cent dispersed spheres would be about 0.6 the diameter of one of the dispersed particles. If the diameter of the carbon black particle is 0.05 micron, the thickness of the film of rubber between the particles would be only 0.03 micron. Layers of rubber only half this thickness strongly adsorbed on the particles of carbon black could substantially immobilize the rubber.

Carbon particles in tread stocks are not uniformly dispersed and are floccu-

lated to a considerable degree. The dispersion of carbon black in such a compound is shown in Figure 5, which is an electron micrograph[6] of a microtome section.

ADSORPTION OF RUBBER BY PIGMENTS

All pigments are able to adsorb rubbers and liquid hydrocarbons to some degree, and this property is developed to a great extent by carbon black. The wetting and adsorption of oil films, together with differences in the surface characteristics, are responsible for the various dispersion and flocculation phe-

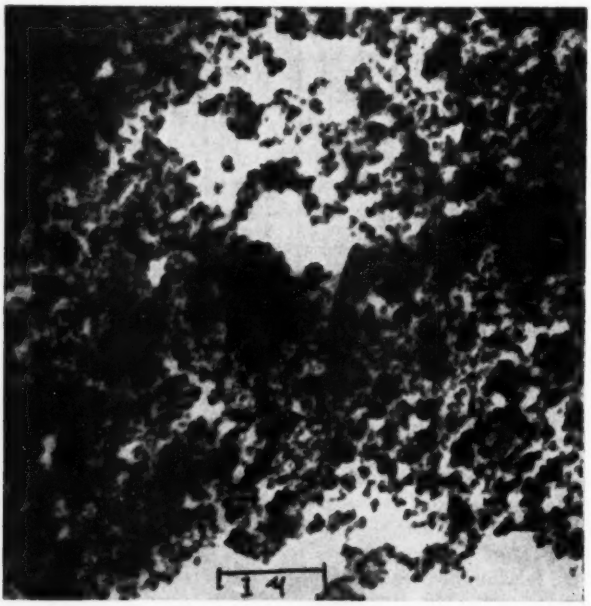

FIG. 5.—Electron micrograph showing dispersion of carbon black in tire-tread stock.

nomena shown predominantly by structure blacks. Voet[7], by measuring the dielectric constant of dispersions under increasing rates of shear, was able to determine the flocculating tendency of different carbons, since the dielectric constant is at a minimum for perfect dispersion. The flocculation is reversible, and the shear required to disperse the carbon is a measure of its tendency to flocculate. The method arranges gas furnace, channel, calcined channel, and acetylene black in this increasing order of flocculating tendency. This is also in the order of increasing electrical conductivity imparted to rubber compounds, but is not in order of either the adsorbing power or the reinforcement of rubber.

The adsorption of rubber from solution by different carbons has been the subject of considerable experimental work[8]. This work has been done with a variety of carbons and solvents. Kolthoff, Gutmacher, and Kahn conclude that GR-S sorbs most easily from the poorest solvents. Duke and Taft find that more polymer is bound if a higher conversion polymer is used. These conclusions appear consistent since the high-conversion polymers tend to be-

come less soluble, although Kolthoff finds that a range between molecular weights of 32,000 and 230,000 is not sufficient to produce significant differences in sorption. Kolthoff, working with polymers in which the amount of styrene varied from zero to 100 per cent, concluded that unsaturation has little effect as long as some unsaturation remains. It is difficult to draw quantitative conclusions from this work because the morphology and solubility of the polymers must change with the styrene content. Schaeffer and coworkers working with a variety of carbons conclude that adsorption of saturated hydrocarbon involves forces of a van der Waals nature, but that adsorption of unsaturated hydrocarbons involves forces of a higher order.

Adsorption from solution involves competition of solvent and carbon for the rubber. This might be of little importance if only monomolecular layers were involved, but the rubber adsorbed from solution is sufficient to provide layers many molecules thick. Rubber bound by direct milling of carbon with

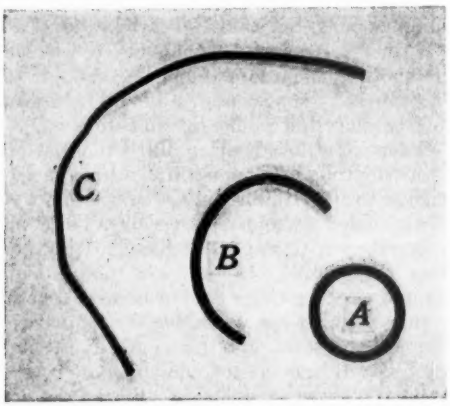

FIG. 6.—Immobilization of unvulcanized rubber by carbon black: A, unbroken ring of unvulcanized gum rubber; B, broken ring of unvulcanized pure gum compound; C, broken ring of unvulcanized compound containing 50 parts of carbon black; note that high elongation has been retained with this compound.

rubber may be as much as ten times that sorbed from solution. Sweitzer and Lyon[9] have altered the procedure of sorption from liquids to include the step of evaporation to dryness, followed by treatment with the original volume of solvent. This procedure increases the amount of bound rubber.

Adsorbed films are seldom monomolecular layers, but may be many molecules thick. This fact is shown by the amount of vapors adsorbed on smooth surfaces of solid powders and by the immobilization of liquids containing dispersed material. The thickness of chloroprene films immobolized by dispersed water particles is of the order of 0.1-micron[10]. Unvulcanized rubber containing carbon black is immobilized in a similar manner[11]. Rings of unvulcanized gum rubber, when stretched at the speed of the usual rubber testing machine, break and return nearly to the unstretched elongation. Rubber containing 50 per cent of its weight of carbon stretches to a high elongation and retains this elongation when the ring breaks. This point is illustrated in Figure 6.

THE CONCEPT OF ORGANIZED RUBBER

Vulcanization unquestionably requires some type of bonding between the rubber molecules. Evidence exists to indicate that this bonding is not of only one type, but may be an actual covalent bonding to produce an insoluble rubber or may be a bonding involving forces of a lower order to produce a vulcanizate which can be peptized[12]. In any case the molecules of rubber must be in a favorable position relative to one another before bonding is possible and, since rubber, unlike liquids or gases, is a relatively immobile material, arrangement of the molecules into favorable positions does not readily occur. If an efficient vulcanization is to be accomplished, the favorable positioning of the molecules must either exist naturally in the rubber or be brought about by some very strong force external to the rubber molecule.

An organized rubber is typified by smoked sheets. This rubber vulcanizes to lose its plasticity and produce high tensile strength in the absence of pigments, and the organized structure is shown by the x-ray diffraction pattern produced by the stretched rubber. The production of a pattern requires not only that the molecules become parallel, but that the carbon atoms are superposed in a regular manner. If, in the straightening process, the molecules tend to slide with respect to one another, some force must be available to stop this motion once the carbons are correctly superposed. Such a force would most likely be found in the regularly recurring points of unsaturation, although saturated polymers such as Vistenex produce a sharp diffraction pattern. If such forces are operative, it is most probable that natural rubber molecules are normally produced by the tree in this condition and are in position to be bonded. Such coiled bundles of molecules or folded and coiled large molecules could be straightened and superposed during stretching to produce some degree of organization between these units. In any case, the units appear to be superposed in such a manner as to be quite readily bonded together.

Neoprene and Butyl rubber are examples of organized synthetic rubbers. Each vulcanizes without the addition of pigments, and each produces an x-ray pattern when stretched. Butadiene-styrene copolymers are typical examples of unorganized rubbers. These products, when mixed with sulfur, zinc oxide, and accelerators, combine with sulfur and become insoluble, but do not develop sufficient tensile strength to be commercially valuable. These rubbers do not show an organized structure by producing an x-ray diffraction pattern.

Unorganized rubbers vulcanize to produce useful physical properties when fine powders and particularly carbon black are added. Incorporation of carbon black produces an unvulcanized compound, with normal plastic properties and with the rubber largely immobilized. Vulcanization now takes place with normal addition of sulfur, but with a great increase in modulus and tensile strength indicating that the manner of addition of the sulfur has been altered.

One effect of added pigments is to improve the efficiency of the vulcanization. This improvement takes place with a wide variety of pigments, but to the greatest extent with carbon black. The improvement produced by carbon black is a function of its surface area; coarse thermal carbons are no better than such different pigments as zinc oxide or coprecipitated lignin. The improvement then parallels the amount of bound rubber.

Adsorption forces may vary from the van der Waals' type to forces of a much higher order. Forces of a higher order which are able to produce insolubility must be associated with the double bonds, since no such results are produced with saturated hydrocarbons such as mineral oils or other high molec-

ular-weight saturated hydrocarbons. The forces may be electrostatic in nature and produce a layering of adjacent reactive positions in the adsorbed molecules of rubber. In this manner, the unorganized rubbers could assume sufficient organization to permit bonding.

Such an organizing effect is not confined to unorganized rubber, but takes place to a less extent with natural rubber. This organizing effect produced by carbon black in smoked sheets is sufficiently great to reestablish the insolubility characteristic of unmilled crepe rubber. Menadue[13] very clearly demonstrated this effect in a series of experiments which deserve more recognition. He showed that the incorporation of a number of powders, such as magnesium carbonate and zinc oxide, which could be later dissolved out by acids, left rubber which produced more viscous solutions or which was largely insoluble. The milling action was necessary to produce the full effect.

Conversely, organized rubbers may be disorganized to a considerable extent simply by swelling with oil before vulcanization[14]. The slight separation of rubber units caused by the addition of 25 parts of soluble oil decreases bonding and gives a vulcanized rubber with low modulus. The addition of the oil after vulcanization does not produce a marked decrease in modulus.

It can be concluded that pigments contribute to the reinforcement of rubber in more than one manner. One effect is purely mechanical, and results in the rubber functioning at a higher elongation than the mixture as a whole. A second effect is due to adsorption of the rubber to hold it securely to the pigment particle. This increases the range of elongations over which the various increments of rubber will work. The third and most important effect appears to be an organizational effect which permits more efficient cross-bonding of the molecules during vulcanization. All these effects vary in magnitude, depending on the type of matrix and type of pigment.

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PHYSICAL PROPERTIES OF NATURAL AND SYNTHETIC RUBBER MATERIALS AT LOW TEMPERATURES *

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In the past few years both government and industrial rubber laboratories have been actively engaged in developing elastomer materials that will function properly under low temperature service conditions. Extensive research programs carried out by these laboratories have resulted in the formulation of a considerable number of low temperature-resistant stocks, such as those used in hose, rubberized fabrics, and gaskets. At the same time many different types of apparatus and procedures have been devised for evaluating the low-temperature properties of the stocks. Each of these tests was, naturally, favored by the organization responsible for its development. This condition resulted in the adoption of a large variety of testing instruments, many of which were designed for use in evaluating the same basic properties, although by slightly different means.

In view of the importance of standardization of evaluation procedures to be incorporated in procurement specifications, the Bureau of Ships, Department of the Navy, authorized the Material Laboratory, New York Naval Shipyard, to investigate all known devices and procedures used in evaluating the low-temperature properties of rubber materials and, if considered desirable, to modify or revise appropriate ones. The over-all objective of the program was to select and standardize equipment and procedures considered to be the most suitable for incorporation in military procurement specifications. An analysis of the manner of employing the major number of rubber items in shipboard low-temperature service shows the following physical properties to be the most significant: (1) flexibility, or the magnitude of stress required to produce an observed degree of deformation; (2) compression set, including the rate and amount of dimensional recovery of a material after being held under constant deformation; and (3) brittleness or structural failure under rapid deformation. The significance of these properties may vary from one application to another, each specification thus requiring the evaluation of the property or properties pertinent to the service performance of the material.

REVIEW OF TEST PROCEDURES

A review was made of the methods used in evaluating the three classes of properties. The second property, compression set, is usually evaluated after the specimens have been aged at elevated temperatures under constant deflection[1]. A basically similar method has been adopted and standardized by the Navy for carrying out low temperature evaluations, a modification being made in that the dimensional recovery of the specimen is evaluated at the test

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temperature and at two time intervals, *viz.*, 10 seconds and 30 minutes after the specimen is released from the clamping plates. In this manner both the rate and amount of recovery of the specimen are evaluated, and the data so obtained can be used in differentiating between first- and second-order transition effects. The evaluation of the third property, brittleness, has likewise been more or less standardized, although there are a number of different instru-

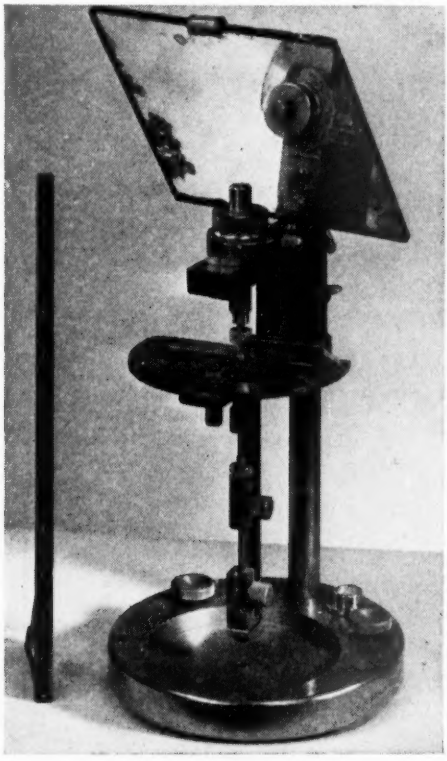

FIG. 1.—Gehman torsional test apparatus. Material Laboratory modification.

ments designed to conform to the procedural requirements[2]. Despite the differences between the several brittleness testers[3], such as the manner of operating the impact component and the number of specimens evaluated at one time, the basic features of these instruments are standard. These standard features are the velocity and dimensions of the impacting component and the amount and manner of deflection of the specimen.

A very considerable number of flexibility tests for evaluating the first property have been developed and reported. These tests are based on various methods for producing deformation. Some require deformation of the specimen by bending, either as a cantilever beam[4] or as a centrally loaded, end-supported beam[5]. Other tests require that the specimens be subjected to tensile

elongation[6], compression-deflection[7], indentation under variable or constant loads[8], or torsional deformation[9]. Some of the apparatus and procedures represent considerable improvement over earlier devices, while others are in use in individual laboratories on the basis of precedence or by the grace of origin only. For these reasons, it was necessary to conduct individual investigations on flexibility, indentation, and similar specimen deformational procedures.

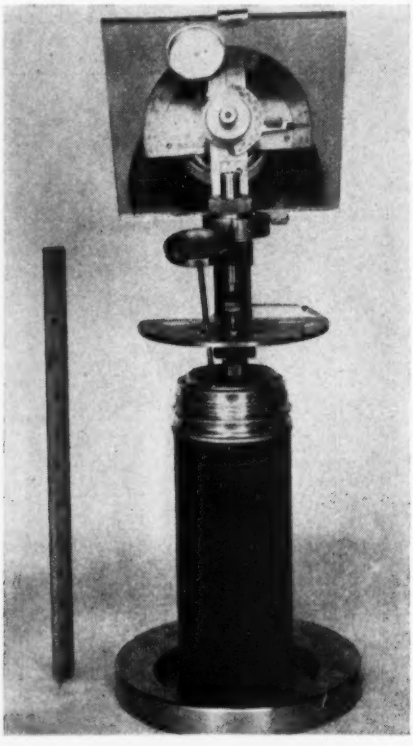

FIG. 2.—Modified Gehman torsional test apparatus. As used in immersion tests.

After this work was completed, most of the testing devices were eliminated from further consideration on the basis of inaccuracy, complexity of operation, or excessive size or cost of the equipment. Of the remaining devices, two were selected for further study.

TORSIONAL APPARATUS

The first of these instruments was the torsional apparatus developed by S. D. Gehman of the Goodyear Research Laboratory. The instrument and procedure as originally designed have been described[10] and were recently adopted as a tentative ASTM method[11]. Although the Gehman tester showed many advantages over other types of flexibility devices, it was not considered entirely satisfactory. The instrument was therefore modified in order to

eliminate some of the elaborate accessory equipment, to simplify the test procedure, and to improve the accuracy of the test.

The modified apparatus is shown in Figure 1.

The specimen rack was replaced by a permanently fixed lower clamp assembly, the upper clamp or grip being suspended from the torque wire as in the original instrument. By this arrangement the zero pointer setting and speci-

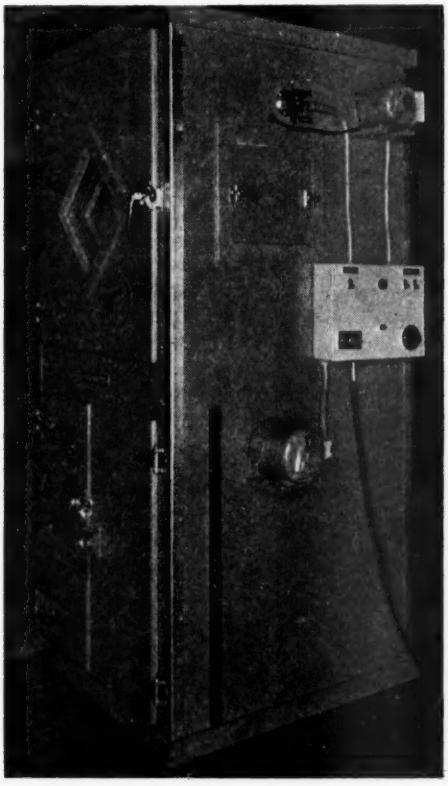

FIG. 3.—Low-temperature test chamber. Material Laboratory design.

men span length can be easily set and will remain properly adjusted during the course of a test. A check on the zero setting of the instrument is made by mounting a metal bar of rectangular cross-section in the specimen grips, making sure that the rotating head and specimen angle indicator are set to zero, and noting the indicator reading after removing the metal bar from the grips. If the angle indicator remains at zero under these conditions, no twist was present in the wire and the instrument is properly adjusted in this respect. The distance between the specimen grips, which determines the span length, can be accurately adjusted by means of gauge blocks.

A Dewar flask containing a mixture of methanol and dry-ice chips was used in cooling specimens exposed to short-time conditioning tests, as shown in

Figure 2. An accurately calibrated Weston thermometer was used in lieu of the original temperature-measuring equipment, and a stop watch was substituted for the electrical timer-light signal. A spirit level was attached to the base of the instrument to permit vertical alignment of the specimen grips, and a mirror was mounted over the torsion head assembly to facilitate reading the deflection scale when the tests are conducted in a thermostatically controlled low-temperature conditioning cabinet. This cabinet, shown in Figure 3, is of the dry-ice refrigerant type, and was designed and constructed in the Material

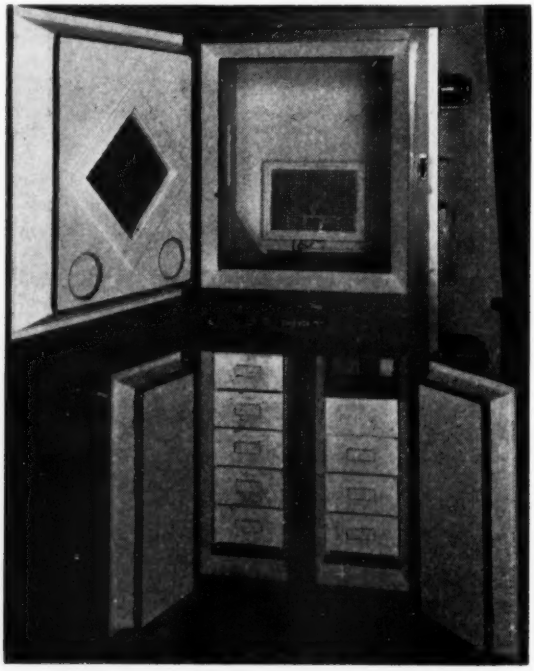

FIG. 4.—Interior view of low-temperature test chamber.

Laboratory for use in carrying out relatively long-time conditioning tests on rubber.

As shown in Figure 4, the specimen-conditioning chamber is in the upper half of the cabinet, while the lower part contains wire-mesh screen trays for holding chunks of dry ice. The blower shown in the right-hand part of the dry-ice section is thermostatically controlled to circulate air from the conditioning chamber down through the stack of trays on the left-hand side and up through the trays on the right. The fan located toward the top of the specimen-conditioning chamber is operated continuously during a test in order to assure attainment of thermal equilibrium conditions therein. The Gehman instrument was operated in the working chamber of the cabinet without the Dewar flask in making long-time specimen conditioning tests.

EXPERIMENTAL PROCEDURES AND CALCULATIONS

In order to evaluate the effects of short-time low-temperature exposure on different elastomers, a specimen of rectangular cross-section is mounted in the jaws of the instrument and the entire upper assembly is lowered, permitting the specimen and grips to be immersed in the cold methanol bath. After the specimen has been conditioned for 3 to 5 minutes in the cold methanol, the torsion head of the tester is rotated and the resulting deformation of the specimen is observed. When the same specimen is used in a series of tests, the relative changes in stiffness of the material at increasingly lower temperatures may be determined without reference to the specimen dimensions. In order, however, to determine numerical or relative values of moduli of different materials under the same conditions, the specimen dimensions must be measured and the moduli calculated as shown below.

$$T = \frac{ab^3\mu G\theta}{L} \tag{1}$$

$$G = \frac{E}{2(1 + m)} \tag{2}$$

$$E = \frac{3TL}{ab^3\mu\theta} \tag{3}$$

$$E = \frac{3c(180 - \phi)L360}{ab^3\mu 2\pi\phi} \tag{4}$$

$$E = \frac{K(180 - \phi)}{\phi} \tag{5}$$

Equation 1 expresses the basic relationship[12] between the torque, T, the cross-sectional dimensions of the specimen, a and b, a factor μ, based on the ratio of a and b, the modulus of rigidity, G, the total angular deformation of the specimen in radians, θ, and the specimen span length, L. Assuming Poisson's ratio, m, to be constant and having a value of 0.5 for elastomers, then the modulus of elasticity, E, as expressed in Equation 3 may be derived from Equations 1 and 2. Expressing the torque, T, in terms of the wire constant, c, and the angle of twist in degrees, ϕ, in lieu of radians, θ, Equation 4 is obtained. This equation was used in calculating the modulus of elasticity of stocks tested in the present investigation. As previously indicated, it may not be necessary in many instances to calculate the numerical values of moduli in order to determine the degree of change in stiffness or flexibility of a material with change in temperature or time of exposure. Using the same or identical specimens in the various tests, Equation 4 may be simplified as indicated in Equation 5, K being a combined constant representing all the individual constants in Equation 4. The ratio E/K is proportional to E and equal to the ratio $(180-\phi)/\phi$. The latter term may, therefore, be called a modulus proportionality factor. This factor is obtained by a simple calculation after noting the specimen twist, ϕ. The change in modulus proportionality factors determined under different conditions using the same or equivalent specimens would then indicate the change in stiffness of the materials.

A series of stocks including Neoprene, Buna-S, Perbunan-26, Hevea, Butyl, Thiokol-FA, and Silicone type of polymers having formulations indicated in

Table I was evaluated using the modified torsional tester. Short-time exposure tests were made in which specimens were conditioned in cold methanol at various low temperatures down to −100° F. In the case of the long-time exposure evaluations, the specimens were conditioned at −20° F in the dry ice cabinet, the tests being made after specimen exposure periods of from 1 to 94 hours.

TABLE I

FORMULATIONS OF MARE ISLAND RUBBER LABORATORY COMPOUNDS

Hevea Stock	E-13-92	GR-S Stock	E-162-489
Smoked sheet	100.0	GR-S	100.0
Zinc oxide	5.0	Zinc oxide	5.0
Stearic acid	1.0	Philblack-A (HMF)	50.0
Cottonseed oil	2.5	Heliozone	3.0
Heliozone	3.0	Tributoxyethyl phosphate	5.0
Age-Rite resin D	1.0	Plasticizer-SC	5.0
Captax	0.5	Dioctyl phthalate	5.0
Altax	0.5	Diisobutyl adipate	5.0
Tuads	0.5	Thionex	2.0
Sulfur	0.75	Diphenylguanidine	0.4
P-33 (FT)	1.0	Sulfur	0.6
Total	115.75	Total	181.0
Perbunan Stock	**E-194-388**	**GR-M Stock**	**E-156-315**
Perbunan-26	100.0	GR-M	100.0
Zinc oxide	5.0	Zinc oxide	1.0
P-33 (FT)	30.0	XLC magnesia	4.0
Statex-B (FF)	30.0	Thermax (MT)	20.0
Bardol	10.0	Paraffin	2.0
Cumar P-10	10.0	Neophax-A	10.0
Stearic acid	1.0	Circo L.P. oil	15.0
Heliozone	3.0	Stearic acid	1.0
Tuads	3.0	Neozone A	2.0
Captax	2.0		
Vandex	0.1		
Total	194.1	Total	155.0
GR-I Stock	**E-34-104**	**Thiokol-FA Stock**	**E-53-17**
GR-I	100.0	Thiokol-FA	100.0
Zinc oxide	4.0	Zinc oxide	10.0
Stearic acid	3.0	Pelletex (SRF)	65.0
Philblack-A	30.0	Stearic acid	0.5
Circo L.P. oil	10.0	Plasticizer-SC	5.0
Tuads	1.0	Tributoxyethyl phosphate	5.0
Captox	0.5	Altax	0.3
Polyac	1.0	Diphenylguanidine	0.1
Sulfur	2.0		
Total	152.2	Total	185.9

TORSIONAL TEST RESULTS

The modulus proportionality factors for the several materials were calculated from the data obtained and are shown in graph form in Figure 5. The factors plotted here were determined in the short-time exposure tests. The Perbunan-26 stock exhibits pronounced stiffening at a temperature of about −20° F, while the Neoprene and Thiokol-FA materials show a large increase

in stiffness on reaching a temperature of about −40° F. The Buna-S and Butyl compounds are roughly midway in the scale of short-time exposure serviceability, while the Hevea and Silicone materials show very little increase in modulus until reaching exposure temperatures of about −50° and −80° F, respectively.

The results of the short-time conditioning tests, however, do not serve as a satisfactory index of the suitability of an elastomer for continued use at low temperatures. As shown in Figure 6, the Thiokol-FA stock exposed for 94

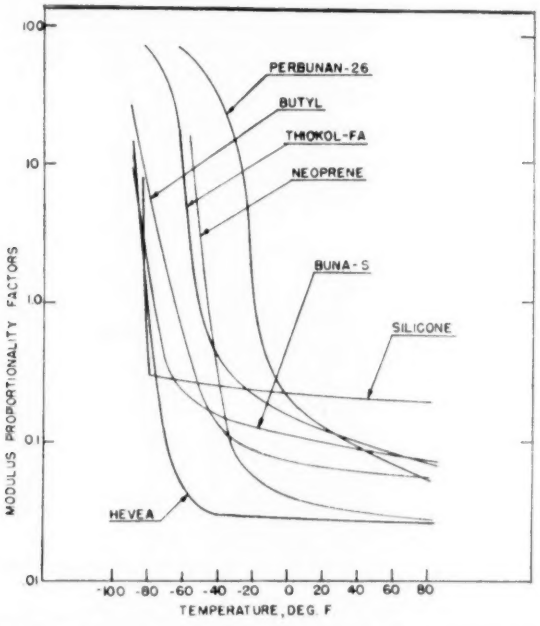

FIG. 5.—Torsional modulus properties of elastomers at low temperatures. Conditioning time 3 to 5 minutes.

hours at −20° F exhibits a rapid increase in the modulus proportionality factor within the first 20 hours of exposure, the value being almost constant after this time. The Hevea compound shows a very pronounced and continued increase in modulus during the entire exposure period, no doubt due to the occurrence of crystallization of the material. Also, the Perbunan-26 stock exhibits a high but relatively constant value for modulus proportionality factor, while the Neoprene elastomer shows a fairly low but gradually increasing modulus value during the entire exposure period. The remaining stocks, *i.e.*, Silicone, Buna S, and Butyl, do not show any significant change in modulus under the stated conditions of test.

The ratio of the modulus factor of a specimen determined at a particular base temperature to that determined after the specimen has been exposed at some low-service temperature may be used as an index of the relative suitability of the material under low-temperature service conditions. The selection of the

temperature and period of exposure will depend largely on the expected service requirements for the material.

HARDNESS INDENTATION APPARATUS

The second and last instrument to be discussed is the Admiralty rubber meter shown in Figure 7. This constant load indentation instrument was constructed in the Material Laboratory, and is in compliance with the British Standards method[13].

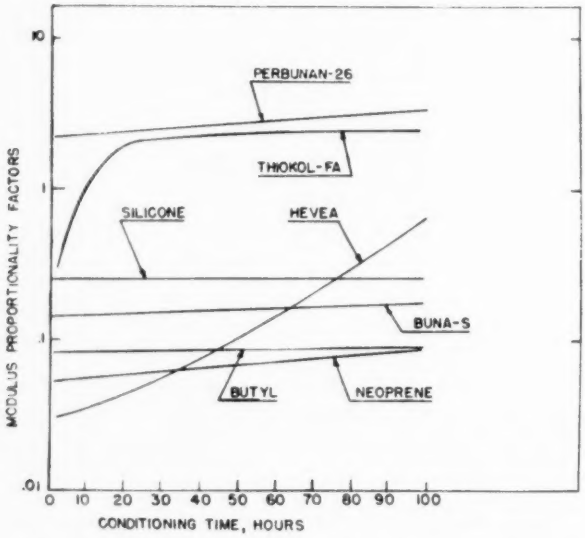

FIG. 6.—Torsional modulus properties of elastomers at low temperatures. Conditioning temperature −20° F.

EXPERIMENTAL PROCEDURES AND CALCULATIONS

The relationship between constant load hardness indentation and the flex modulus of rubber materials has been investigated by Scott[14] among others. Scott found that this relationship may be expressed by Equation 6:

$$E = \frac{A}{H^{1.35}} \tag{6}$$

In Equation 6, A is a constant determined by the physical characteristics of the instrument, *viz.*, the indentor and the major load. It follows from Equation 6 that, for a particular instrument using the same indentor and major load in all tests, a modulus proportionality factor equal to E/A may be expressed by Equation 7.

$$\frac{E}{A} = \frac{1}{H^{1.35}} \tag{7}$$

Hardness indentation tests were made at 75° F using specimens of the compounds previously discussed. The modulus proportionality factors obtained

by use of the term $(180-\phi)/\phi$ in the case of the Gehman apparatus and the term $1/H^{1.35}$ in the case of the hardness tester were then calculated and plotted, as shown in Figure 8.

In view of the linearity of the graph, which confirms the previously expressed relationship, further tests were conducted to investigate the existence of this relationship at low temperatures.

The Admiralty instrument was modified as shown in Figure 9. The major

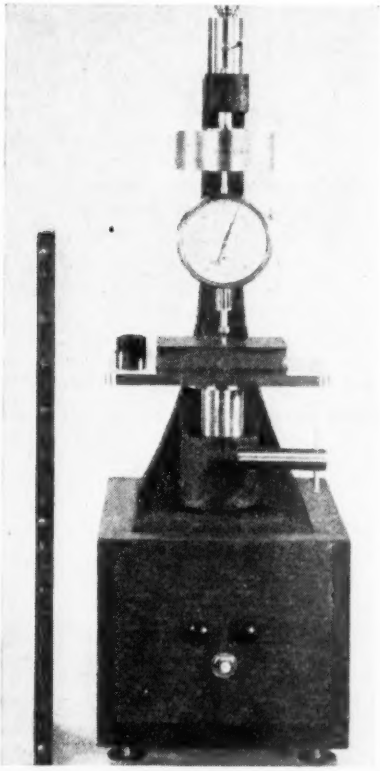

FIG. 7.—Admiralty rubber meter. Specimen subjected to major load indentation.

load was changed to 1000 grams and the indentor to 0.125-inch diameter, the instrument thus being in conformity with ASTM standard method[7] and Federal specification[15]. A cylindrically bored weight was placed on the specimen concentric with the indentor to ensure contact between the specimen and the support plate. A series of 12 stocks prepared by the Office of Rubber Reserve and having formulations indicated in Table II was used in the tests in which both Gehman torsional data and hardness indentation data were obtained, using the modified Gehman and Admiralty instruments. Specimens were conditioned for 94 hours at temperatures ranging from 75° down to −50°

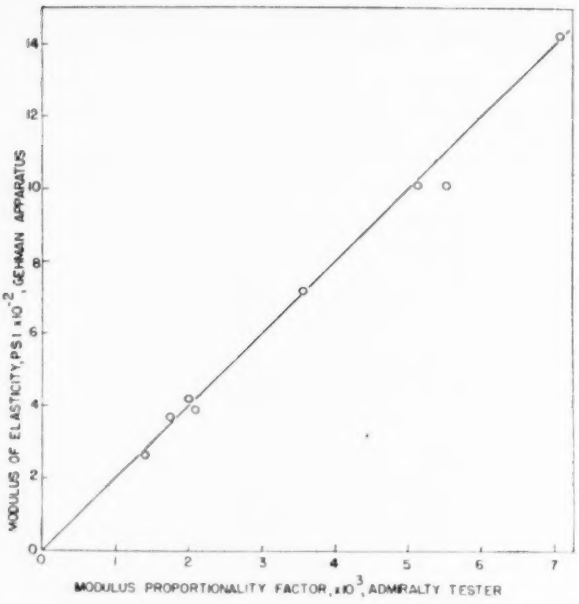

FIG. 8.—Relationship between flex modulus and indentation modulus at 75° F.

TABLE II

FORMULATIONS OF OFFICE OF RUBBER RESERVE COMPOUNDS

	1 Natural rubber	2 GR-S X-539	3 122° F Polybd XP-148	4 14° F Polybd XP-169	5 Na Polybd 81PC4-6
Polymer	100	100	100	100	100
Statex-B	40	40	40	40	40
Zinc oxide	5	5	5	5	5
Sulfur	3	2	2	2	2
Altax	0.75	1.75	3	3	1.25
Stearic acid	3		1.5	1.5	3
PBNA	1.5				
Final weight	153.25	148.75	151.5	151.5	151.25

	6 Na 75/25 Bd/S	7 Perbunan 26	8 85/15 Bd/S XP-138 122° F	9 80/8/12 Bd/I/S 41° F
Polymer	100	100	100	100
Statex-B	40	40	40	40
Zinc oxide	5	5	5	5
Sulfur	2	1.25	2	2
Altax	1.25	1.75	3	3
Stearic acid	3		1.5	1.5
Final weight	151.25	148.00	151.5	151.5

TABLE II—*Continued*

10 GR-S		11 85/15 Bd/S (XP-138) 122° F		12 Perbunan 26	
Polymer	100	Polymer	100	Polymer	100
Philblack-A	40	Statex-B	75	Statex-B	75
Zinc oxide	5	Zinc oxide	5	Zinc oxide	5
Heliozone	1	Plastolein-905C	10	Adipol-BCA	10
Flexol-TOF	20	Dicapryl sebacate	10	Dibutyl sebacate	10
Methyl Tuads	0.8	Stearic acid	1	Plasticizer-3425	10
Sulfur	1	Methyl Tuads	1	Stearic acid	1
		Sulfur	1	Thionex	0.3
				Sulfur	1.5
Final weight	167.8		203.0		212.8

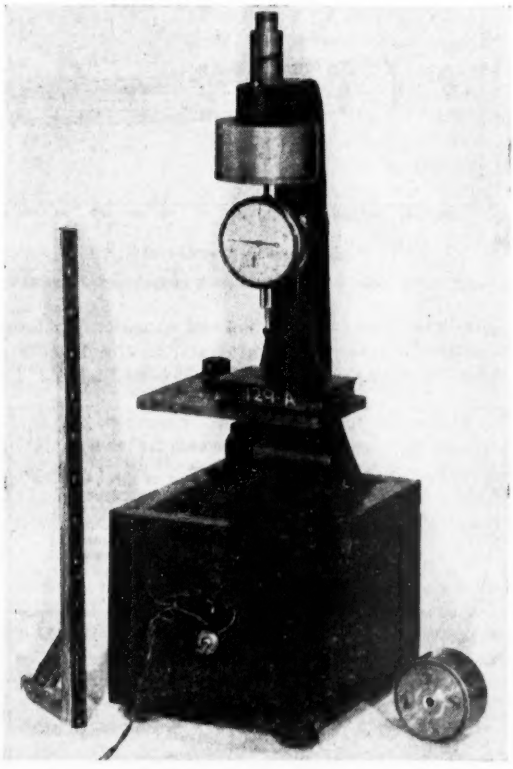

FIG. 9.—Admiralty indentometer.

F. The values for flex moduli of the various stocks were calculated and are presented graphically in Figure 10. The sodium-catalyzed 75/25 butadiene-styrene material, an unplasticized Perbunan-26 compound (No. 394-S-7) and

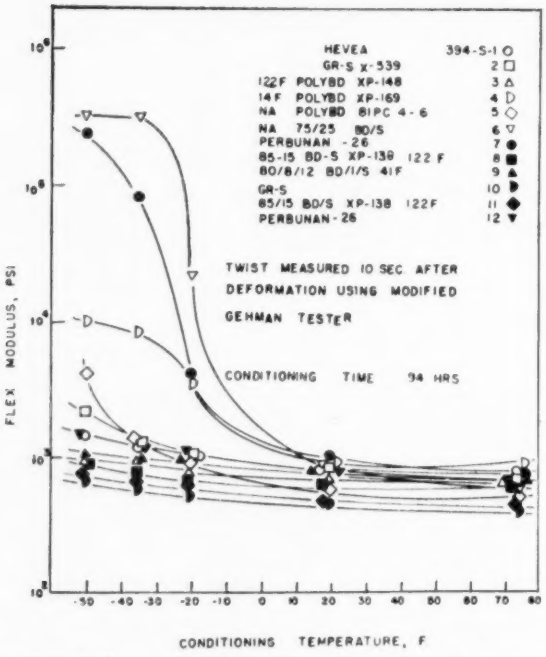
HEVEA 394-S-1
GR-S X-539 2
122F POLYBD XP-148 3
14F POLYBD XP-169 4
NA POLYBD 81PC 4-6 5
NA 75/25 BD/S 6
PERBUNAN -26 7
85-15 BD-S XP-139 122 F 8
80/8/12 BD/I/S 41F 9
GR-S 10
65/15 BD/S XP-138 122F 11
PERBUNAN-26 12
TWIST MEASURED 10 SEC AFTER DEFORMATION USING MODIFIED GEHMAN TESTER
CONDITIONING TIME 94 HRS
FLEX MODULUS, PSI
CONDITIONING TEMPERATURE, F

FIG. 10.—Change of flex modulus with conditioning temperature of various elastomers.

the 14° F polybutadiene compound all showed considerably larger increases in modulus at progressively lower temperatures than the other materials, which included a plasticized Perbunan-26 stock (No. 394-S-12), a 122° F polybutadiene

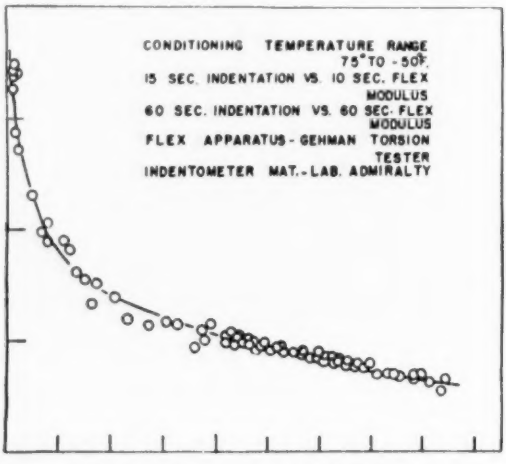
CONDITIONING TEMPERATURE RANGE 75°TO -50°F.
15 SEC. INDENTATION VS. 10 SEC. FLEX MODULUS
60 SEC. INDENTATION VS. 60 SEC. FLEX MODULUS
FLEX APPARATUS - GEHMAN TORSION TESTER
INDENTOMETER MAT.-LAB. ADMIRALTY

FIG. 11.—Relationship between constant load hardness indentation and flexural moduli of various elastomers.

stock, and plasticized and unplasticized GR-S materials. The plasticized GR-S and the plasticized 122° F 85/15 butadiene-styrene compounds showed the lowest increases in modulus.

HARDNESS TEST RESULTS

The flex modulus and hardness indentation data of the Office of Rubber Reserve compounds, determined at comparable intervals after deformation, were plotted as shown in Figure 11. The semi-log plot shows the relationship between flex modulus and hardness indentation to be represented by a hyperbolic function of the form $y = cx^n$. A log-log plot of the data over the range of indentations from 1.7 to 0.1 mm. and of flex modulus from 350 to 20,000 pounds per square inch is shown in Figure 12. Evaluation of the equation on

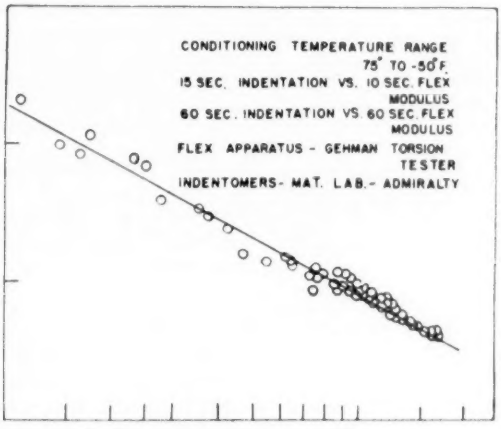
CONDITIONING TEMPERATURE RANGE
75° TO -50° F.
15 SEC. INDENTATION VS. 10 SEC. FLEX MODULUS
60 SEC. INDENTATION VS. 60 SEC. FLEX MODULUS
FLEX APPARATUS - GEHMAN TORSION TESTER
INDENTOMERS- MAT. LAB.- ADMIRALTY

FIG. 12.—Relationship between constant load hardness indentation and flexural moduli of various elastomers.

the basis of the plot shows the relationship to be expressed by the equation $E = 820/H^{1.36}$. This equation is similar in form to that determined by Scott, the exponent being very close, and it shows the basic equivalence of flex stiffness and resistance to indentation. The relationship appears to be valid for various types of compounds and over a relatively wide range of specimen exposure conditions.

CONCLUSION

A torsional apparatus and a hardness indentation tester have been found to be essentially equivalent for use in evaluating the stiffness characteristics of elastomers over a range of low temperatures. The torsion apparatus, requiring the use of relatively small specimens, facilitates carrying out various conditioning cycles on a material, such as liquid immersion or atmospheric aging. The indentometer, on the other hand, permits the employment of larger sized specimens or even samples, such as relatively thick gasket stocks. There are, then, individual advantages in each apparatus which would determine the choice to be made in selecting a test method for a particular specification.

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APPARATUS FOR THE MEASUREMENT OF THE DYNAMIC SHEAR MODULUS AND HYSTERESIS OF RUBBER AT LOW FREQUENCIES *

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INTRODUCTION

The mechanical hysteresis of rubber has been investigated in a number of different ways. A review of most of the literature on this subject prior to 1946 has been made by Dillon and Gehman[1] and these authors classify hysteresis measurement methods as follows:

(*a*) Low-speed stress-strain loop.
(*b*) Impact resilience.
(*c*) Free vibration.
(*d*) Forced vibration at resonance.
(*e*) Forced vibration: nonresonance.

The apparatus which is to be described is of the last type and has some points of resemblance both to the well known Roelig[2] machine and also to that described by Kornfel'd and Posnjak[3]. The principle of the method is the subjection of a rubber test-piece to a force in simple shear, varying sinusoidally with time, the measurement of instantaneous values of force and displacement by photoelectric pickups, and the display on the screen of a cathode-ray tube of the mechanical hysteresis loop described by the vibrating rubber.

DESCRIPTION OF APPARATUS

Details of the apparatus are shown in Figure 1. An eccentric *A* of adjustable throw is driven from a 1-h.p. electric motor through a variable speed gear box giving output speeds of approximately 1000–0.1 r.p.m. in eight logarithmic steps. By means of a connecting rod *B*, the cam produces a reciprocating motion in a cross head *C*. This motion is approximately sinusoidal; in the least favorable case, with the eccentric adjusted to its maximum throw, it can be shown (see Appendix) that the departure from sinusoidal motion is nowhere more than 4 per cent. The reciprocating motion is transmitted by a rigid rod to the upper segment of an elliptic spring *D*, the lower segment of which is rigidly coupled to a carriage *E*. The rubber test-piece consists of two rubber cylinders *F* bonded to either end of a cylindrical steel block, and this central block is locked securely into the carriage. The outer ends of the rubber cylinders are bonded to steel end-plates, which are clamped securely to the base casting of the apparatus. The elliptic spring has a linear load/deformation characteristic, and its compliance in a vertical sense is at least 100 times that of the rubber test-piece and thus, with the machine in motion, the sinu-

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soidal motion of the upper segment of the spring gives rise to a sinusoidal force on the center block of the rubber test-piece.

In order to carry out measurements over a wide range of temperatures, a sheet metal tank (not shown in Figure 1) is attached to the base of the machine so that the test-piece and carriage are completely submerged in a heating or cooling liquid contained in the tank. Using a mixture of alcohol and solid

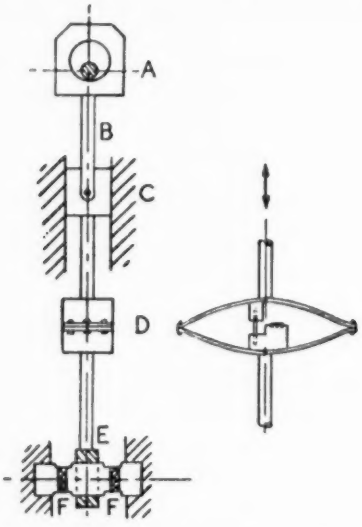

FIG. 1.—Low-frequency dynamic test machine.

carbon dioxide, a temperature of $-60°$ C may readily be attained. A careful check shows that over the whole range of frequency, amplitude, and temperature employed, the viscosity of the containing liquid has a negligible effect on the behavior of the vibrating system.

The deformations of the spring and of the rubber are translated into electrical potentials by a photoelectric system shown diagrammatically in Figure 2. Light from a 6-V 108-W projector lamp H passes through a condenser lens J and a limiting aperture K before striking a semi-reflecting plate L. This plate splits the beam, one component passing through a system of prisms to produce uniform illumination of a horizontal slit S_1. The other component after reflection illuminates uniformly a vertical slit S_2. The whole of the optical system so far described, excluding the slits S_1 and S_2, is enclosed in a light proof aluminum

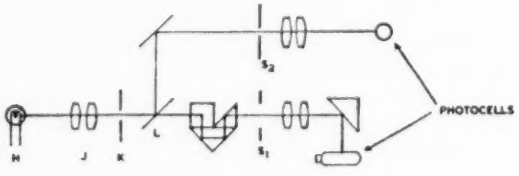

FIG. 2.—Optical system.

casing, from which the two beams emerge through a plate-glass window. Each slit is carried at the end of a tube containing focusing lenses and a photoelectric cell. The light flux falling upon either photocell is proportional to the area of the corresponding slit. The effective area of S_1 is varied by a shutter attached to the center of the lower segment of the elliptic spring and, hence, having the same vertical motion as the rubber carriage, while the effective area of slit S_2 is varied by the motion of two shutters, one attached to the upper and one to the lower segment of the spring, so that any change of the spring deformation produces a proportionate change in the light flux through S_2.

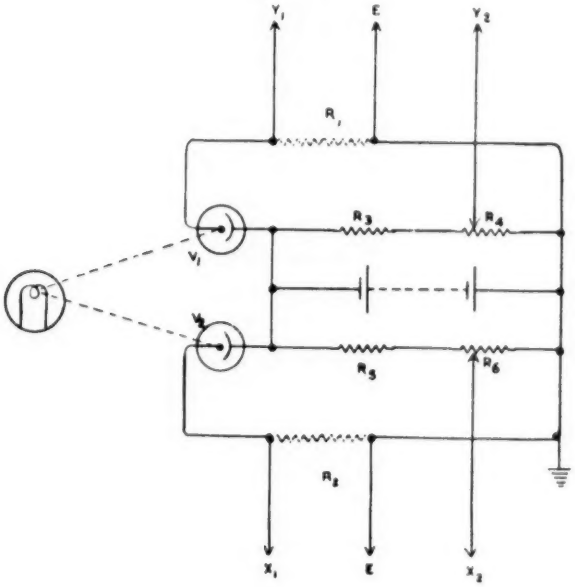

FIG. 3.—Photocells and oscilloscope coupling circuit.

R_1, R_2 = 1.2 MΩ (input resistance of oscilloscope)
R_3 = 5.9 MΩ
R_4 = 50 kΩ
R_5 = 1 MΩ
R_6 = 50 kΩ
V_1, V_2 = 90 AV
Y_1, Y_2, X_1, X_2, E = connections to oscilloscope

The photoelectric cells are connected through the circuits shown in Figure 3 to a cathode-ray oscilloscope having d.c. amplification on both X and Y axes. By means of the controls R_4 and R_6 the d.c. component voltages from the outputs of these coupling circuits are backed off, so that, with the two shutters in their mean positions, the oscillograph spot is in the center of the screen.

The projector lamp is supplied with a current of 18 A at 6 V from a motor generator set with a heavy duty 6 V battery "floating" in the circuit. It is found desirable, when carrying out precise measurements, to run from batteries alone, since the slight ripple superimposed on the d.c. output of the generator causes a small degree of interference with the observed hysteresis pattern.

EVALUATION OF DYNAMIC PROPERTIES OF RUBBER

Results of dynamic mechanical tests have been presented in many different ways, according to the purpose for which the results are required. In a previous publication[4] where a smaller frequency range was considered, the properties were described by reference to a model consisting of a parallel coupled spring and dashpot, and were specified in terms of a dynamic shear modulus and viscosity. In the present case it is found convenient to represent the results, which cover a far wider frequency range, in terms of the dynamic shear modulus and the tangent of the angle of mechanical loss.

If an alternating force

$$y = F \cos \omega t \tag{1}$$

be applied to the rubber test-piece of stiffness S and viscous coefficient K, the following equation holds:

$$K(dx/dt) + Sx = F \cos \omega t$$

where x is the instantaneous deformation. This has the solution:

$$x = F \cos (\omega t - \delta)/(S^2 + \omega^2 K^2)^{\frac{1}{2}} \tag{2}$$

where

$$\delta = \tan^{-1} \omega K/S$$

Equations (1) and (2) define the hysteresis loop, Figure 4. When $x = 0$, $\omega t -$

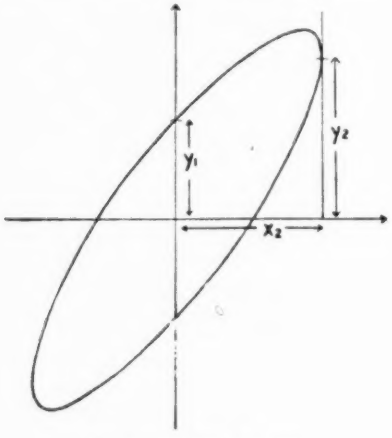

FIG. 4.—The hysteresis loop.

$\delta = (2n + 1)\pi/2$, and $y = F \cos\omega t = \pm F \sin \delta = \pm y_1$. The maximum value of $x = \pm F/(S^2 + \omega^2 K^2)^{\frac{1}{2}} = \pm x_2$. This is given by $\omega t - \delta = n\pi$, then $y = F \cos \omega t = \pm F \cos \delta = \pm y_2$. Now $S = (S^2 + \omega^2 K^2)^{\frac{1}{2}} \cos \delta = y_2/x_2$ and $\tan \delta = y_1/y_2$.

The hysteresis loop and a superimposed zero line along the x-axis are photographed on 35 mm. recorder film and projected through an enlarger with about $\times$ 15 magnification on to graph paper ruled in mm. The elliptic spring having been calibrated by a dead-load method the scales of the x and y oscilloscope deflections are established by reading with a microscope the amplitudes of rub-

ber and spring deformations and comparing these with the corresponding amplitudes of the projected oscillogram. Measurements on the projected hysteresis loop then allow the calculation of the absolute values of quanties x_2, y_1, and y_2.

An alternative method of measuring the angle of loss when this is high is to observe the steady wave forms of deflection and force against time on the screen of the oscilloscope, and measure directly the phase difference. The oscilloscope time base for this purpose is provided by a saw-tooth form voltage signal of the same period as that of the vibration, obtained by driving the moving contact of a full sweep potentiometer directly from the driving shaft of the eccentric.

RESULTS

As an example of the type of result obtained with the above apparatus, reference may be made to the dynamic properties of a Thiokol-RD vulcanizate. The variation of dynamic shear modulus with frequency at several tempera-

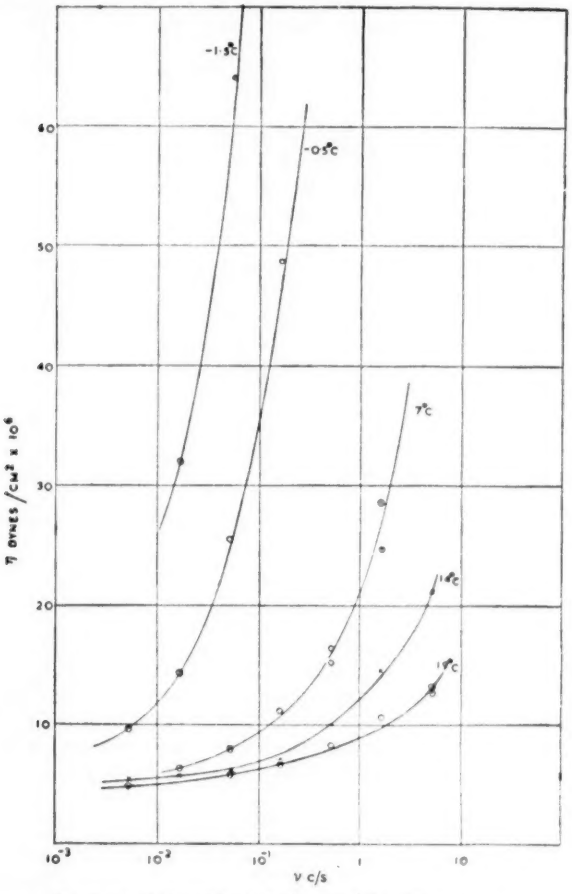

FIG. 5.—Variation of dynamic shear modulus with frequency.

tures is shown in Figure 5, the corresponding measurements of tan δ being given in Figure 6. It will be seen that the tan δ *vs.* ν relationship at $-5°$ C and $-1°$ passes through a sharp maximum. At other temperatures only a single branch of each curve is found within the frequency range employed. In order to avoid confusion, experimental points are not indicated on all curves,

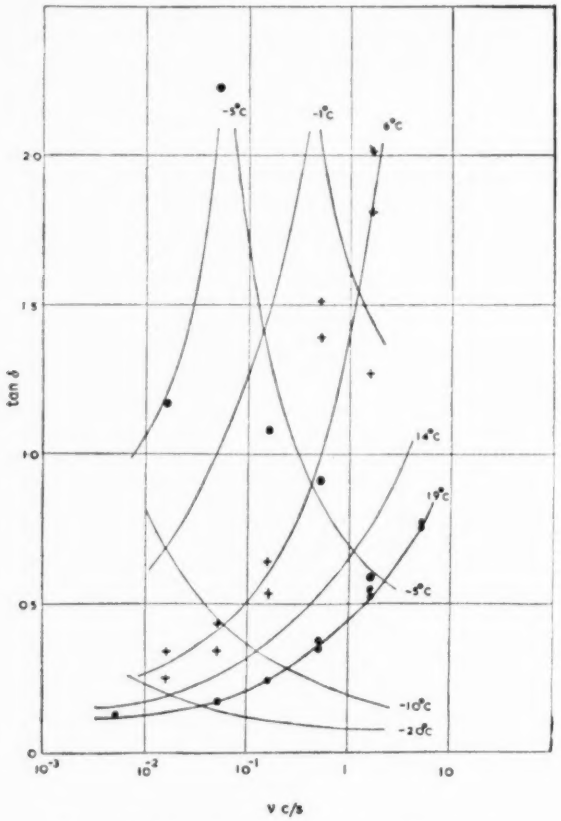

FIG. 6.—Variation of mechanical loss angle with frequency.

but the scatter of the points indicates an increasing experimental error in regions of high tan δ. These results are in general agreement with data previously published for this polymer[5]. The apparatus is in use for the investigation of the pattern of changes in dynamic properties of a range of natural and synthetic rubberlike polymers over a wide range of temperature and frequency. The full results of these measurements will be published elsewhere.

SUMMARY

An apparatus is described which subjects a rubber test-piece to a force in simple shear, varying sinusoidally with time in the frequency range of 0.0017–17 c/s, the instantaneous values of force and displacement being measured by

photoelectric pickups. From the display on the screen of a cathode-ray tube of the mechanical hysteresis loop described by the vibrating rubber, measurements are made which make possible calculation of the dynamic shear modulus and hysteresis. Typical results are given.

ACKNOWLEDGMENTS

Acknowledgment is made to Mr. D. Wilson for assistance in the design of the mechanical parts and to Mr. C. D. Kinloch for the design of the electronic section. This work forms part of a program of technological research undertaken by the Board of the British Rubber Producers' Research Association.

APPENDIX

Departure of the cross-head motion from a true sinusoidal form. For a crank radius r, and a connecting rod length l, we have:

$$x/2r = (1 - \cos\theta)/2 + l[1 - (1 - r^2 \sin^2\theta/l^2)^{\frac{1}{2}}]/2r$$

for the displacement of the cross-head x as a fraction of the total throw, at a crank angle θ. The departure D from the corresponding displacement in the case of a true sinusoidal motion, is given by:

$$D = x/2r - (1 - \cos\theta)/2 = l[1 - (1 - r^2 \sin^2\theta/l^2)^{\frac{1}{2}}]/2r \qquad (1)$$

and is seen, on differentiating the right-hand side of equation (1), with respect to θ, to be a maximum when θ is 90°.

Substituting this value of θ, D is seen to be a monotonically decreasing function of l/r for values of l/r greater than 1. Using the minimum value of the ratio l/r used in practice, approximately 8, we obtain: $D_{max} = 0.0313$.

The departure of the motion from a pure sinusoidal form having the same amplitude is seen never to exceed 4 per cent of the total throw.

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WEAR RESISTANCE OF VULCANIZED ELASTOMERS *

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Many laboratory test machines have been designed to estimate the wear resistance of vulcanized elastomers. Although a few of these machines were developed for special types of rubber products, such as coated fabrics, the greater number have been designed to assess the wearing qualities of vulcanizates intended for use in footwear or automobile tires. The large number of new elastomeric materials and reinforcing pigments introduced in the past decade has increased the need of a reliable method for selecting promising combinations in the laboratory before submitting these to expensive performance tests under simulated service conditions.

Present laboratory methods involve rubbing the vulcanized compound over a surface composed of abrasive particles, such as emery, carborundum, or silica particles, which may be affixed to a paper backing or bonded in a solid matrix. In one method, a relatively flat surface of the specimen is caused to slide over the abrasive surface, and there is continuous contact between these two surfaces throughout the test. This is the method employed with the du Pont[1] and the National Bureau of Standards abraders[2]. In later types of machines, the test-specimen is a wheel of vulcanizate that is driven over a bonded abrasive surface, usually at an angle to the direction of rotation of the abrasive disk. The Lambourn[3] and Vogt[4] machines, examples of this method, are classed as discontinuous tests, since the rotation of the specimen produces an intermittent contact between any area of vulcanizate and the abrasive surface. In all these methods the abrasive surface tends to become clogged with the abraded product, and an air blast is employed to remove this material. In one instance[5], the viscous smear produced on the abrasive surface was so pronounced that the vulcanizate was extracted with ethanol-toluene azeotrope in an effort to eliminate the source of this contaminating material.

The majority of such abrasion methods do give a reasonable correlation with service performance when different types or quantities of carbon black or other fillers are compared with one elastomer. However, they are most unreliable when employed to compare the wear resistance of vulcanizates of different elastomers. This deficiency has hindered the development of new types of elastomers and has prolonged the investigation of possible effects of the various polymerization factors on the wear resistance of the vulcanized product.

Extensive road tests[6] have established that tires of the commercial butadiene-styrene polymer (GR-S) polymerized at 41° F provide 23 per cent greater mileage for equal wear than that prepared at a temperature of 122° F. A laboratory method that would demonstrate this superior wear resistance for a 41° F GR-S vulcanizate might be expected to yield a qualitative evaluation of other variables in the field of butadiene-styrene elastomers. This, then, was made the primary objective of the present investigation.

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TEST PROCEDURES

Except where noted, the GR-S-10, 41° F GR-S, and 122° F GR-S were commercial polymers produced by Canadian Synthetic Rubber, Ltd., Sarnia. The elastomeric compounds were prepared on a 6 × 12-inch laboratory mill, following the compounding schedule outlined in the specifications for government synthetic rubbers.

The test strips were vulcanized in a four-cavity mold which produced a concave test-surface having the same radius of curvature as the test-drum of the National Bureau of Standards abrader.

The determination of the abrasive resistance on garnet paper was carried out according to the A.S.T.M. Designation D394-47, Method B.

The ethanol-toluene extraction treatment was carried out in a Soxhlet extraction apparatus, using a 3½-inch length of test-strip. The treatment consisted of 96 hours' extraction with ethanol-toluene azeotrope, 48 hours' extraction with ethanol (during which the solvent was changed three times), followed by air-drying for 24 hours at 77° F.

The acetone extraction procedure consisted of placing a 3½-inch length of test-strip in 200 cc. of acetone in a sealed pint can for 48 hours at 77° F. The strip was removed and allowed to dry in the dark for 24 hours in air at 77° F.

In all the tests carried out on abrasive paper, the specimen was cemented to a piece of vulcanized fiber backing, by which it was fastened to the test arm.

The ball penetration was measured at an ambient temperature of 77° F, using a minor load of 30 grams and a major load of 1030 grams, on a ⅛-inch ball bearing.

The 30-mesh stainless steel screen was cut parallel to the wire to give a sheet 6 inches wide. This sheet was formed over the surface of the drum, so the cut ends overlapped by about ¾ inch and the wires ran around the circumference of the drum parallel to the edge of the test-specimen. The screen was fixed in this position by means of metal straps. The metal surface of the test drum was coated with a commercial reclaimed rubber cement to prevent the screen from slipping during a test run. The test was carried out in a conditioned room at an ambient temperature of 77° F and relative humidity of 50 per cent. A stream of air was blown onto the screen through the air duct of the National Bureau of Standards abrader so that it was directed at right angles to the axis of rotation of the drum. An air pressure of 10 pounds per square inch gage was used at the entry to the air duct.

The test-specimen was cut from the molded test strip to give a 1 × 1 inch sample. A metal frame was bolted to the underside of the test-arm of the abrader, in which a 1 × 1 inch opening was cut in the ⅛-inch thick metal. The surface of the specimen was roughened with sandpaper and then fitted into the frame holder on the test arm. The specimen was broken in for 2000 to 2500 revolutions of the drum at a speed of 40 r.p.m., removed, cleaned of loose particles of vulcanizate, and weighed.

The drum was allowed to revolve with the air blast directed onto the screen in order to reduce the temperature of the metal wire to 77° F. before the start of the next test run. The specimen was replaced in the frame holder in exactly the same position as before, and a test run was carried out for exactly 2500 revolutions. The specimen was cleaned, weighed, and the wear resistance calculated as the number of kilorevolutions required to remove 1 cc. of vulcanizate, indicated as krev./cc.

EXPERIMENTAL

The initial tests were carried out on the National Bureau of Standards abrader, using No. 2½ garnet abrasive paper. The GR-S elastomers were compounded in the specification recipes prescribed by the Office of Rubber Reserve, 122° F GR-S in recipe A and 41° F GR-S in recipe B (Table I). With the

TABLE I

TEST RECIPES

	Parts	
	A	B
122° F GR-S	100	—
41° F GR-S	—	100
EPC carbon black	40	40
Zinc oxide	5	5
Stearic acid	—	1.5
Altax	1.75	3
Sulfur	2	2

standard weight of 0.328 kg. on the test-arm, the abrasive resistance of the 122° F GR-S vulcanizate was found to be 79 per cent greater than that of the 41° F GR-S. The consensus is that when service conditions are more severe, the 41° F GR-S shows a greater margin of superiority over 122° F GR-S. When the load on the test-arm (Table II, Figure 1) was increased, the abrasive

TABLE II

EFFECT OF TEST LOAD ON ABRASIVE RESISTANCE

(No. 2½ garnet paper)

Load on test arm (kg.)	Abrasive resistance (krev./cc.)	
	41° F GR-S[a]	122° F GR-S[b]
0.154	0.67	1.10
0.200	0.60	1.00
0.328	0.47	0.84
0.481	0.40	0.65
0.655	0.35	0.53
0.987	0.24	0.42
1.295	0.16	0.32

[a] Polysar Krylene compounded in recipe B; press cure 60 minutes at 292° F.
[b] Polysar S compounded in recipe A; press cure 50 minutes at 292° F.

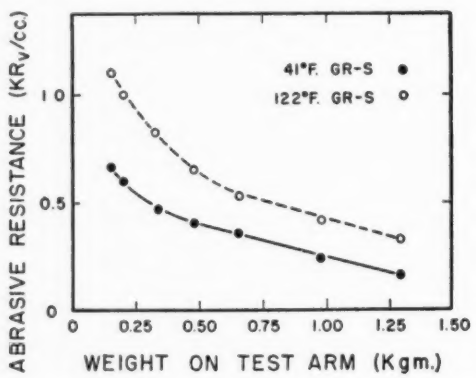

FIG. 1.—Effect of test load on abrasive resistance. Rubber Reserve recipe; 2½ garnet paper.

resistance of both vulcanizates decreased and that of 41° F GR-S approached the value shown by the 122° F GR-S vulcanizate. However, there was no clear indication of a change in the relative abrasive resistance of the two elastomers, at least up to a load which produced excessive vibration of the specimens during the test.

The effect of a prior extraction of the vulcanizate with ethanol-toluene azeotrope was examined for 122° F GR-S vulcanizates containing 30, 40, and 60 parts of EPC carbon black per 100 parts of rubber. This time consuming procedure takes 7 days and concurrently, duplicate specimens were immersed in (1) acetone and (2) ethylene dichloride for 48 hours at 77° F. All these immersion treatments produced a drop in the hardness of the vulcanizate (Table III). The specimens treated with ethanol-toluene azeotrope suffered

TABLE III

EFFECT OF VARIOUS SOLVENTS ON EXTRACTED ABRASIVE RESISTANCE

Conditions: 122° F GR-S in Recipe A
Press cure, 70 min. at 292° F
Abrasive surface, 2½ garnet paper

Treatment	EPC Black, (parts/ 100 rubber)	¼-inch ball penetration (mils)	Abrasive resistance (krev./cc.)	Abrasive rating[a], (%)
None	30	86	0.65	100
	40	70	0.88	100
	60	43	1.10	100
Ethanol-toluene Azeotrope	30	91	0.27	41
	40	77	0.39	44
	60	55	0.51	46
Acetone	30	105	0.48	73
	40	86	0.60	69
	60	80	0.80	73
Ethylene dichloride[b]	30	104	0.74	114
	40	85	0.99	113
	60	64	1.05	96

[a] Compared to untreated vulcanizate of the same EPC carbon black loading.
[b] Allowed to air-dry for 5 days at 77° F.

the greatest loss in abrasive resistance, and even those immersed in acetone showed a substantial decrease in this property. The percentage decrease in abrasive resistance was remarkably constant for each solvent.

The vulcanizates of three synthetic elastomers (Table IV) showed about the same percentage decrease in abrasive resistance after acetone immersion. The GR-S-10 vulcanizate, however, produced a heavy black smear on the abrasive paper in the original condition, and this abnormally high value was reduced to a "normal" level after treatment with acetone. This was the only contamination of the abrasive paper observed during this program. The acetone treatment reduced the abrasive resistance of the GR-S-10 vulcanizate and, then, it showed the same qualitative rating with respect to GR-S as has been reported for road tests[7]. The two 41° F GR-S elastomers, however, had a lower abrasive resistance than that of 122° F GR-S, both in the original and treated conditions.

The comparative abrasive resistance of 41° and 122° F GR-S had not been unduly influenced by the state of cure of the vulcanizates, since it was found that this factor had only a minor effect on the abrasive resistance of the acetone-treated vulcanizate (Table V).

TABLE IV

RELATIVE WEAR OF ELASTOMERS ON 2½ GARNET PAPER

Elastomer	122° F GR-S	GR-S-10	41° F GR-S	X-485
Polymerization temp. (° F)	122	122	41	41
Test recipe	A	B	B	B
Press cure at 292° F (min.)	60	60	60	60
Abrasive resistance (krev./cc.)				
Original	1.02	3.75[a]	0.54	0.56
Acetone-treated	0.72	0.61	0.45	0.45
Treated index (original = 100)	71	14	84	80
Ball penetration (mils)				
Original	74	83	70	71
Acetone treated	91	100	86	87
Change	+17	+17	+16	+16

[a] Produced a smear on the abrasive paper.

Newton and Scott[8] have reported that significant differences in relative abrasive resistance may be obtained by using different sizes of abrasive grit in tests with the du Pont abrader. The vulcanizates of 41° F and 122° F GR-S were tested on various grades of abrasive paper (Table VI, Figure 2). The

TABLE V

EFFECT OF TIME OF CURE ON ABRASIVE RESISTANCE OF EXTRACTED VULCANIZATE

Polymer	X-485		
Recipe	B		
Immersion treatment	48 hours in acetone at 77° F		
Drying treatment	24 hours in air at 77° F		
Abrasive material	2½ garnet paper		
Press cure at 292° F (min.)	35	50	70
No. tests	58	58	58
Abrasive resistance (krev./cc.)			
Mean value	0.374	0.383	0.385
Standard deviation of individual test	0.041	0.037	0.040

two vulcanizates showed an equal abrasive resistance on 4/0 garnet paper and the 41° F GR-S vulcanizate was somewhat superior on a 5/0 garnet paper. Unfortunately there was excessive vibration of the specimen on this fine grit, and it was difficult to obtain reproducible test values.

TABLE VI

EFFECT OF ABRASIVE GRIT SIZE ON RELATIVE ABRASIVE RESISTANCE OF 41° AND 122° F GR-S

Abrasive paper		Abrasive resistance, (krev./cc.)		Comparative rating of 41° F GR-S
Grade	Mesh size of grit	41° F GR-S[a]	122° F GR-S[b]	(122° F GR-S = 100)
2½	30	0.52	0.79	66
1/0	80	0.43	0.62	69
2/0	100	0.56	0.69	81
3/0	120	0.64	0.66	97
4/0	150	1.00	0.94	106
5/0	180	1.37	1.26	109

[a] Recipe B; press cure, 60 minutes at 292° F.
[b] Recipe A; press cure, 50 minutes at 292° F.

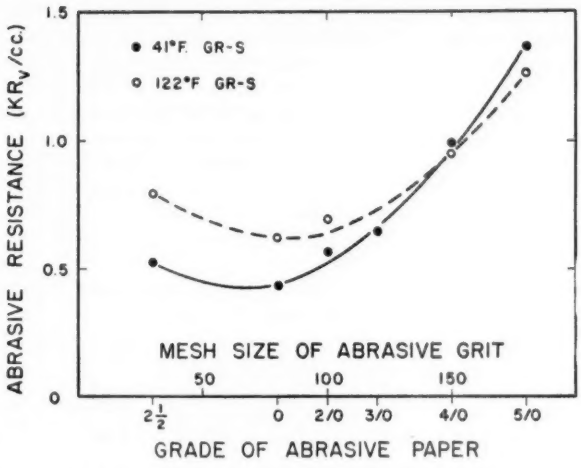

FIG. 2.—Effect of abrasive grit size on abrasive resistance.

In an effort to determine the cause of this reversal in the relative resistance of the two polymers, a measurement was made of the temperature of the specimens during a test on 2½ garnet paper. A copper-constantan thermocouple was cemented between the specimen and the vulcanized fiber backing material, and the temperature at this point was noted during a run (Figure 3). The temperature of the 41° F GR-S vulcanizate was found to be about 8° F higher

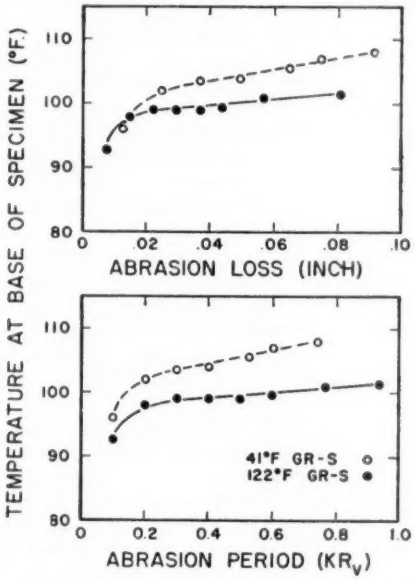

FIG. 3.—Temperature rise at base of test specimen. Rubber Reserve recipe; 2½ garnet paper; ambient temperature, 77° F.

than that of the 122° F elastomer, even at a distance of about 0.2 inch from the plane of abrasive action.

A search was made for a surface that would produce a lower rate of wear of the vulcanizate and, preferably, allow a more rapid dispersion of the heat generated during abrasion. A steel screen might offer some advantages as a test surface. A run was made with a 30-mesh stainless steel screen, and it was found that the vulcanizate was worn by movement over the screen and at a rate considerably lower than that observed on an abrasive grit surface. The 41° F GR-S vulcanizate showed a higher wear resistance on the 30-mesh screen than that of the 122° F elastomer, and the same relative order of wear resist-

SCREEN	SCREEN MESH SIZE	WIRE DIAMETER (INCH)	WIRE SPACING (INCH)	WEAR RESISTANCE (KR_v/cc.) 41°F. GR-S	122°F. GR-S	RELATIVE RATING (122°F. GR-S ×100)
A	10	0.0470	0.0530	4.05	2.55	159
B	30	0.0130	0.0203	9.95	5.82	171
C	100	0.0045	0.0055	5.05	3.46	146
D	—	0.0330	0.0670	7.94	5.72	139

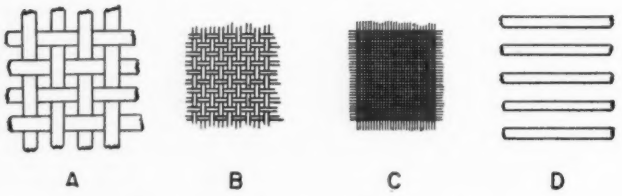

FIG. 4.—Wear resistance on various wire surfaces.

ance was found on 10-mesh and 100-mesh stainless steel screens. The ideal surface might consist of a series of wires, uniformly spaced, whose length ran at right angles to the direction of rotation of the drum. Indeed, such a test surface had a considerable wearing effect on the vulcanizate, and the 41° F GR-S vulcanizate, again, showed more resistance to wear than that of the 122° F GR-S. The test data are shown in Figure 4, which also gives a schematic representation of the various test surfaces. The differences in the value of wear resistance obtained on the various screens would seem to be a function of the area of contact of the vulcanizate and steel during each revolution of the drum, and, perhaps, of the spacing of the wire. The 30-mesh screen produced the largest difference in the wear resistance of the two elastomers, and it was adopted for use in subsequent tests.

This screen consisted of a 28 × 30-mesh, single-crimped, having a wire, 0.0135 to 0.015 inch diameter, of Type 304 stainless steel. The profile of the screen, then, would be different in the directions of the warp and shoot wires; this is illustrated in Figure 5. In the warp direction (*B*) the 122° F GR-S vulcanizate was found to have a wear resistance some 30 per cent of that in the direction of the shoot wires (*A*). In each case the surface of the specimen was worn to produce a series of alternate ribs and grooves. The grooves were

formed by the points at which the warp and shoot wire crossed in the screen. The *A* direction was selected for use in subsequent tests.

Three screens were cut in the *A* direction, and the average wear resistance of the 122° F GR-S vulcanizate was 16.00, 16.13, and 15.40 krev. per cc. loss of

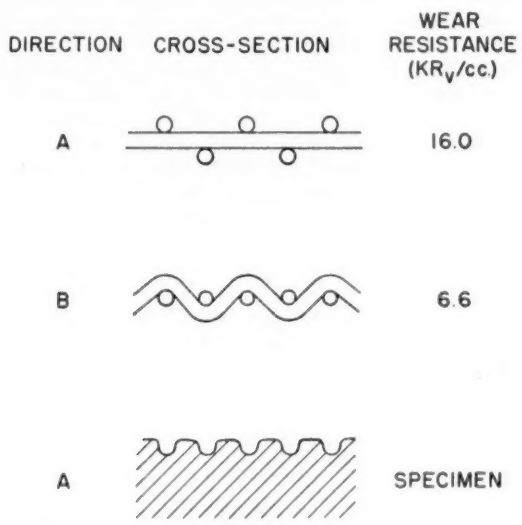

FIG. 5.—Cross-section of screen and specimen.

vulcanizate. One screen was heated in a muffle for 5 minutes at 550° C in order to burn off any organic material; after a short break-in period, a value for wear resistance similar to that of the original test was obtained. One of these screens was used in various tests for 750,000 revolutions of the test-drum and, after this time, further specimens of the 122° F GR-S vulcanizate gave a wear resistance some 3 per cent lower than in the original test. One might assume that continued wear of the screen would flatten the top of the wires, thus increasing the area of contact between the steel and vulcanizate during each revolution. This should result in an increased rate of wear of the vulcanizate,

TABLE VII

CONSECUTIVE TESTS OF ONE SPECIMEN
(30-mesh screen)

Test	Revolutions	Loss (gram)	Wear resistance (krev./cc.)
1	2000	0.0633	36.4
2	2000	0.0624	36.9
3	2000	0.0596	38.7
4	2000	0.0672	34.3
5	2239	0.0679	38.1
6	2097	0.0628	38.6
7	2600	0.0779	38.7
8	2002	0.0581	39.9
9	2145	0.0611	39.9
10	2195	0.0665	38.1

and is the direct opposite of that which occurs with an abrasive paper. Here the abrasive grit is rapidly worn or rubbed off the backing material, with an accompanying rapid increase in the apparent abrasive resistance of the vulcanizate.

In the previous tests of the 30-mesh screen a period of 2500 revolutions of the test-drum (about 1 hour) had been adopted on an arbitrary basis; a depth of about 0.01 inch of the vulcanizate was removed in one test. It seemed pertinent to determine if the value calculated from such a small loss of vulcanizate would be reproducible between tests of the same specimen. The test data (Table VII) show that a good reproducibility was obtained for one test-specimen in a series of consecutive wear periods.

In all these tests, an air blast had been directed at the screen, using an air pressure of 7 pounds per square inch gage at the entry to the distribution duct of the National Bureau of Standards abrader. Since any contaminating material derived from contact with the vulcanizate could easily be swept off the wires into the interstices of the screen, it seemed desirable to determine what effect, if any, was now being produced by the air blast. Accordingly, a 122° F GR-S tread vulcanizate, containing 5 parts of Paraflux per 100 parts of rubber was tested on the 30-mesh screen, using an undercure and a cure approximating the optimum tensile cure. The data (Table VIII) show that there

TABLE VIII

EFFECT OF AIR ON WEAR RESISTANCE

(30-mesh screen)

	Wear resistance, (krev./cc.)		Relative wear resistance (%)	
	Cure[a] (35 min.)	Cure (70 min.)	Cure (35 min.)	Cure (70 min.)
No air	2.39	4.34	100	100
Air directed at screen				
7 lb./sq. inch gage	3.03	6.28	127	145
10 lb./sq. inch gage	3.34	6.86	140	158
Air directed at specimen				
10 lb./sq. inch gage	3.10	5.65	130	130

[a] Cures at 292° F.

is considerable increase in the wear resistance of the vulcanizates when an air stream is directed onto the screen at right angles to the axis of rotation of the drum. The wear resistance increased as the air pressure at the entry to the distribution duct was increased from 7 to 10 pounds per square inch gage. A further test where the air stream was directed at the specimen itself resulted in a slight decrease in wear resistance. This effect would seem to result from the difficulty in causing the air to reach the interface of the specimen and the screen. The surface of the screen itself became warm during a test run, and it is probable that the air blast served to reduce the temperature of the screen and the surface of the specimen. The data (Table XII) indicated that the maximum wear resistance was obtained at an air pressure of 10 pounds per square inch gage. Possibly a still higher value would be obtained at higher air pressures, but the change in wear resistance, using air pressures of 7 and 10 pounds per square inch gage, did not indicate that there would be any substantial gain at higher air pressures.

A comparison of 41° and 122° F GR-S vulcanizates was made in tread-type recipes containing 0, 1, 2.5, and 5 parts of Paraflux per 100 parts of rubber.

For any one compound, the wear resistance increased with the time of cure, and reached a maximum level at cure time somewhat longer than the optimum tensile cure (Table IX). The relationships of tensile strength, modulus at

TABLE IX

EFFECT OF PARAFLUX ON WEAR RESISTANCE OF 41° AND 122° F GR-S

		Parts		Parts
Base recipe:	Polymer	100	Zinc oxide	3
	EPC black	50	Santocure	1.25
	Paraflux	As shown	Sulfur	1.80
	Stearic acid	2		

	41° F GR-S			122° F GR-S		
	Wear resistance, (krev./cc.)	Modulus at 300% (lb./sq. inch)	Tensile strength (lb./sq. inch)	Wear resistance (krev./cc.)	Modulus at 300% (lb./sq. inch)	Tensile strength (lb./sq. inch)
Cure[a] without Paraflux (min.)						
35	8.0	730	3820	21.4	1650	3650
50	27.4	1320	4480	36.8	2100	3710
70	44.3	1750	4680	39.3	2250	3430
100	48.3	2030	4400	40.6	2350	3200
140	47.8	2220	4600	42.5	2450	3315
Cure with 1 part Paraflux (min.)						
35	8.8	750	3800	20.8	1550	3730
50	23.6	1350	4820	31.4	1960	3505
70	39.7	1610	4545	38.3	2320	3740
100	43.8	1870	4310	41.9	2330	2310
140	36.8	2010	4470	37.6	2280	3220
Cure with 2.5 parts Paraflux (min.)						
35	Undercured	590	3915	15.0	1315	3830
50	17.2	1100	4460	30.3	1580	3625
70	—	1450	4370	30.7	1740	3265
100	37.2	1680	4535	41.1	1820	2890
140	37.9	1780	4420	—	1835	3140
Cure with 5 parts Paraflux (min.)						
35	Undercured	520	3755	11.1	1185	3160
50	10.2	880	4380	18.0	1540	3800
70	18.2	1170	4340	22.0	1675	3650
100	25.1	1340	4510	28.8	1755	3720
140	28.3	1460	4420	25.3	1860	3220

[a] All cures at 292° F.

300 per cent, and wear resistance with the time of cure are illustrated in Figure 6. Each of these values increased with an increase in the state of cure of the vulcanizate.

The maximum wear resistance values were estimated from the data given in Table IX and the values for 41° and 122° F GR-S vulcanizates are compared in Figure 7. At all levels of softener, up to 5 parts per 100 parts of rubber, the 41° F GR-S vulcanizates showed superior wear resistance to the corresponding 122° F GR-S vulcanizate. The wear resistance of the vulcanizates decreased with an increase in the loading of softener, but a greater change was produced in the wear resistance of the 41° F GR-S than the 122° F GR-S.

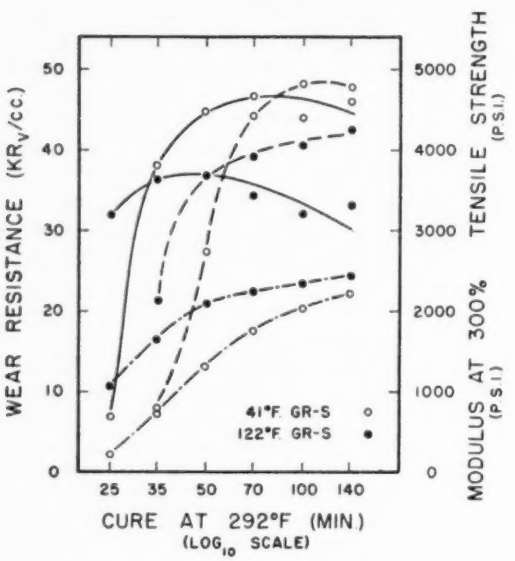

FIG. 6.—Wear resistance - - -; modulus at 300% — - —; and tensile strength —— of 41° and 122° F GR-S vulcanizates.

Under the test load, the vulcanizate is deformed around the wires of the screen, and thus a stiffer vulcanizate would rub over a smaller area of wire during one revolution of the drum. If the modulus at 300 per cent is proportional to the deformation of the vulcanizate, the wear resistance of these two polymers should vary directly with the modulus of their vulcanizates. A relationship (Figure 8) was indicated between these two properties for each cure,

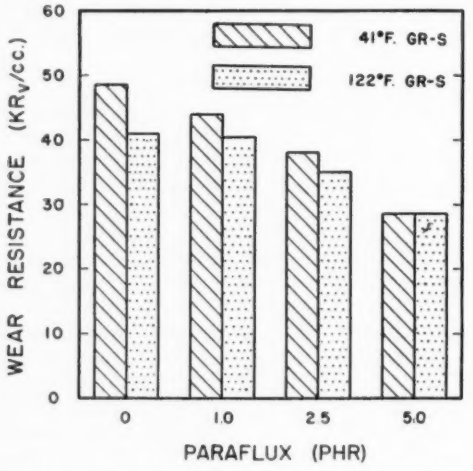

FIG. 7.—Effect of Paraflux on relative wear resistance of 41° and 122° F GR-S vulcanizates.

at each softener loading. From these curves, the wear resistance of the 41° F GR-S vulcanizates was calculated to be about 160 per cent of that shown by a 122° F GR-S vulcanizate of the same modulus at 300 per cent. This is an approximate value, since the two values were measured on test-pieces cured at

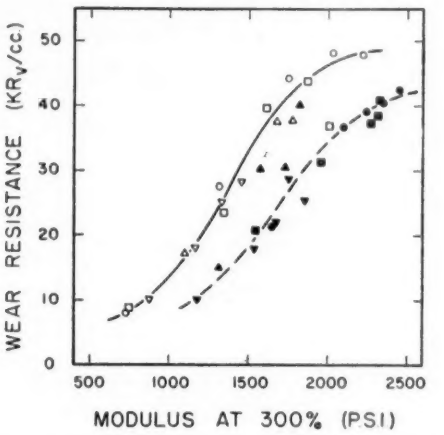

FIG. 8.—Correlation of wear resistance and modulus at 300%.

Paraflux (parts/100 rubber)	GR-S 41° F	GR-S 122° F
0	○	●
1.0	□	■
2.5	△	▲
5.0	▽	▼

different times in mold cavities having different dimensions. It does suggest, however, that good correlation would be obtained if both tests could be carried out on the same vulcanized specimen.

The presence of a maximum in the wear resistance-time of cure curve was more evident in compounds showing a high wear resistance, such as those con-

TABLE X

WEAR RESISTANCE OF 41° F GR–S WITH VARIOUS LOADINGS OF SILENE EF

		Parts		Parts
Recipe:	41° F GR-S	100	Zinc oxide	5
	Silene EF	As shown	Altax	4
	Cumar MH2½	10	Sulfur	2
	Stearic acid	2		

Cure at 292° F (min.)	Silene EF (parts) 22.5	30	60	90
	Wear resistance (krev./cc.)			
20	0.45	0.39	0.73	1.69
25	0.45	0.63	1.38	2.38
30	0.55	0.72	1.64	2.68
35	0.57	0.75	1.65	2.90
50	0.62	0.74	1.72	3.05
70	0.58	0.72	1.58	2.86

taining an HAF carbon black, and, in this case, the effect of state of cure was found to be more critical.

As illustrated by the data in Table X and Figure 9, the 30-mesh screen may also be employed to evaluate the wear resistance of soling-type compounds.

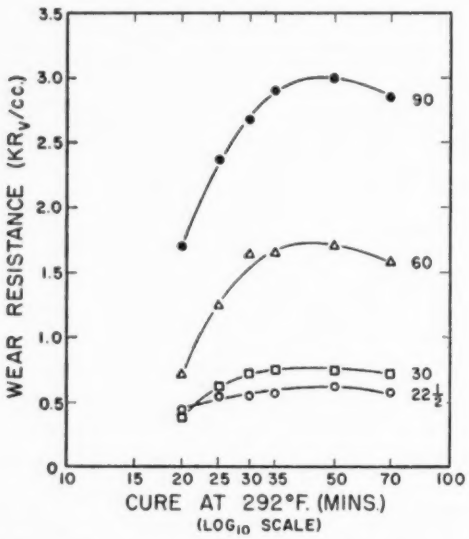

FIG. 9.—Effect of Silene EF on wear resistance of 41° F GR-S vulcanizates. Parts/100 rubber: Polysar Krylene, 100; Silene EF, as shown; Cumar MH 2½, 10; stearic acid, 2; zinc oxide, 5; Altax, 3; sulfur, 2.

Up to at least 90 parts of Silene EF per 100 parts of rubber in a 41° F GR-S compound, the wear resistance was proportional to the filler loading.

The effects of quantity and type of carbon black, and of softener on the wear resistance of 122° F GR-S compounds (Table XI) were similar to that reported for road wear tests[9]. Tests with the 30-mesh screen are very sensitive to variations in elastomer characteristics and test-recipe. The Rubber Reserve

TABLE XI

EFFECT OF CARBON BLACK AND SOFTENER LOADING ON WEAR RESISTANCE OF 41° F AND 122° F GR-S

(30-mesh screen)

Polymer, GR-S	41° F	122° F	41° F	122° F	122° F	122° F	122° F	122° F
Carbon black								
Type	EPC	EPC	EPC	EPC	EPC	SRF	HAF	HAF
Loading[a]	40	40	50	50	50	50	50	50
Softener								
Type	—	—	—	—	Paraflux	Paraflux	Paraflux	—
Loading[a]	—	—	—	—	5	5	5	—
Wear resistance, krev./cc.	9.0	8.5	22.5	17.5	11.5	3.0	28.5	39.4

[a] Parts/100 parts of rubber.

Co. specification recipe, which contains only 40 parts of EPC carbon black per 100 parts of rubber, shows about the same relative wear resistance for 41° F and 122° F GR-S as one containing 50 parts of EPC or HAF carbon black per 100 parts of rubber. Thus, the properties of a small quantity of an experimental elastomer may be compared with those of a commercial elastomer using the Rubber Reserve recipes, and it would not be necessary to prepare a special test compound for this purpose.

As promising as this method may appear, it has one characteristic in common with the other abrasion tests, namely, it would indicate that a natural-rubber tread vulcanizate has a wear resistance considerably lower than that of a comparable GR-S vulcanizate (Table XII). In this test, the abraded surface

TABLE XII

WEAR RESISTANCE OF NATURAL RUBBER TREAD VULCANIZATE

(30-mesh screen)

		Parts		Parts
Recipe:	Smoked sheet	100	Stearic acid	3
	HAF carbon black	50	Agerite HP	1
	Pine tar	5	Captax	0.6
	Zinc oxide	3	Sulfur	2.8

Press cure at 292° F (min.)	Wear resistance (krev./cc.)
20	10.5
25	10.8
35	12.2
50	11.8

of the natural rubber vulcanizate was somewhat sticky and a slight smear was produced on the steel screen. However, the presence of this contamination did not produce a high wear resistance, and the low value may be associated with a high coefficient of friction between a natural-rubber vulcanizate and stainless steel or, possibly, a degradative softening of the vulcanizate accelerated by the high temperature generated at the vulcanizate-steel interface.

SUMMARY

The use of a stainless steel wire screen on the National Bureau of Standards abrader will produce a wearing action on a vulcanized elastomer and 41° and 122° F GR-S vulcanizates exhibit the same relative order of wear resistance that has been observed in road tests.

The wear resistance determined on this surface is sensitive to the state of cure of the vulcanizate, and a maximum value is obtained at a cure slightly longer than the optimum tensile cure. The method is very sensitive to the type and quantity of carbon black and softener loading in the vulcanizate. These factors are ranked also in the same order as observed in road tests. The method may be applied to footwear compounds as well as to tread vulcanizates of synthetic elastomers.

The use of a metal screen offers a uniform and reproducible test surface for determining wear resistance; it suffers little change during continued use; and the material is not affected by minor changes in the ambient temperature or relative humidity.

The reproducible nature of the wire screen greatly reduces the need for a reference standard, and comparisons may be made between tests conducted at relatively long intervals of time on either the same or a duplicate screen.

ACKNOWLEDGMENT

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A TENTATIVE EXPLANATION OF THE WEISSENBERG EFFECT IN LATEX SOLUTIONS *

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Shearing motion produces in certain liquids, not only shearing stresses but also stresses in other directions. This effect, described by Garner and Nissan[1] and by Weissenberg[2], was treated theoretically by Oldroyd[3], Reiner[4], and Rivlin[5]. It will be shown that the last two theories are an oversimplification

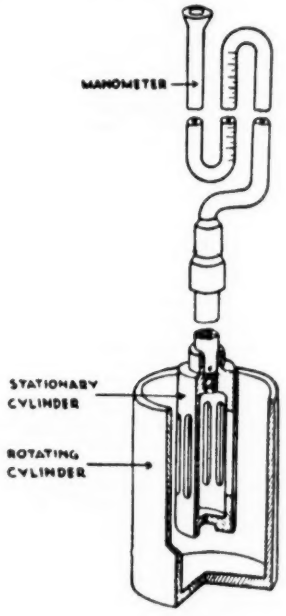

Fig. 1.

and do not describe the more complicated behavior of slightly vulcanized latex solutions.

The instrument constructed for this investigation (see Figure 1) ensures a cylindrical field with only small end effects, which would tend to generate secondary motions constantly transferring liquids from fields of one velocity gradient to another. The outer cylinder is rotated; the inner stationary cylinder has slots through which the liquid can flow. Tangential forces between

* Reprinted from the *Bulletin of the Research Council of Israel*, Vol. 1, No. 3, pages 113–116, August 1951.

the cylinders result in a positive pressure within the inner cylinder. This pressure is transmitted by means of air through a pipe to a glass manometer consisting of an alcohol-filled U-tube.

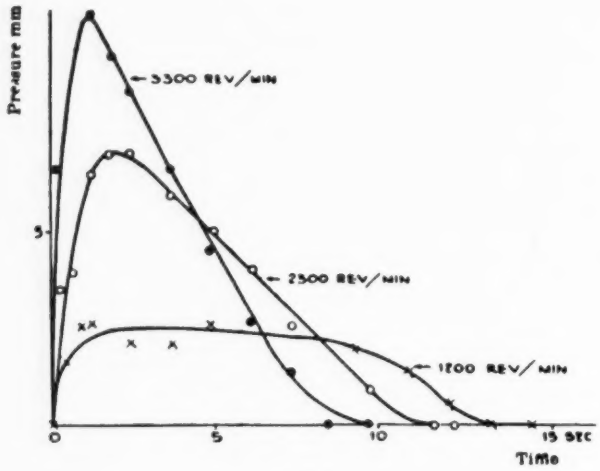

FIG. 2.

The results obtained with slightly vulcanized latex solutions and constant rotation velocity are presented graphically in Figure 2. The pressure rises from zero to a maximum value and drops again nearly to zero. The increase in pressure does not reappear when rotation is interrupted and started again after a short interval. Only after a recovery time of several hours can the initial

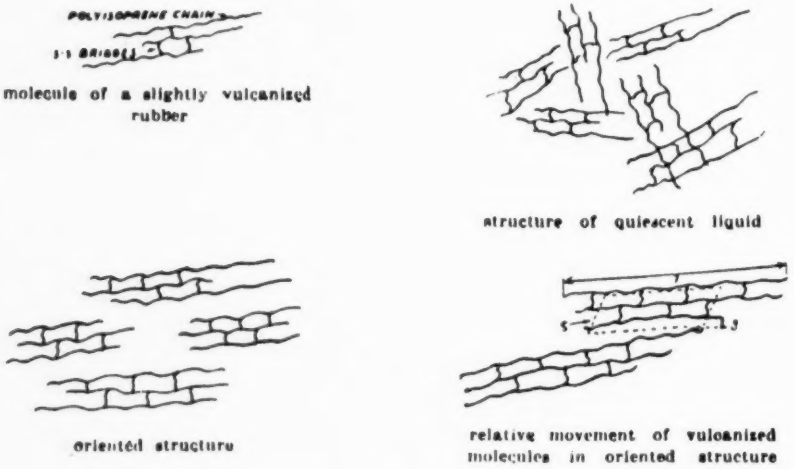
POLYISOPRENE CHAIN
molecule of a slightly vulcanized rubber
structure of quiescent liquid
oriented structure
relative movement of vulcanized molecules in oriented structure

FIG. 3.

phenomenon be observed again. The maximum pressure reached increases with the rotation velocity.

This phenomenon can be interpreted on the basis of the following model: at the start, the molecules form relatively large aggregates of random structure (Figure 3). The time necessary for their formation being of the order of magnitude of 3 to 24 hours, *i.e.*, the time necessary for "recovery." When the liquid is subjected to a rotary movement, some of the aggregates adhere to the solid surfaces and arrange themselves in the direction of the rotary movement, in the way in which macaroni twist around a turning fork. This arrangement of the shearing aggregates produces tangential and radial forces, causing the liquid to raise the pressure in the inner cylinder. (Only the tangential forces are considered here.)

If the velocity gradient increases, the degree of this orientation should also increase. This degree of orientation is measured for sufficiently low gradients by the maximal increase in pressure as depicted in Figure 4.

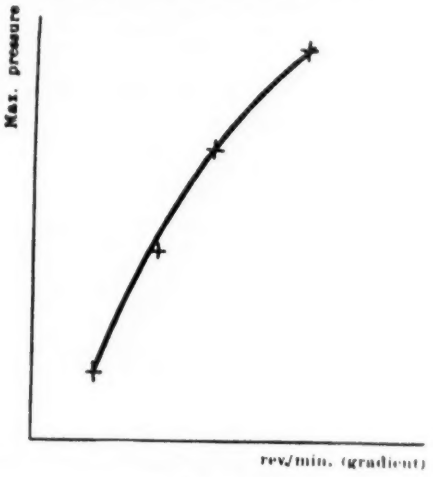

FIG. 5.

As orientation increases, however, another opposing process becomes operative. The shearing stresses developing in the oriented structure tend to overcome the van der Waals forces and thus to destroy the aggregates. With the velocity gradient in these experiments, this degradation process is much slower than the orientation, although much faster than the building-up of the aggregates from their individual elements in solution.

For the breakdown of the oriented structure, the following mechanical model is suggested. Each bundle of oriented molecules can perform two viscous movements: it can participate in the rotation of the liquid as a whole, and can also maintain an interval flow of the constituent elements against each other. When the bundle lies across a velocity gradient, sufficient shear stresses develop to produce a relative movement of the constituent in the molecular aggregate. Eventually, an increasing number of bundles disintegrate. When this effect has reached its final stage, the pressure in the inner cylinder falls to zero.

It is possible, therefore, to speak of two viscosities: the overall viscosity,

measured in the usual viscometer, and an "interior viscosity," determined by the van der Waals interaction between the constituent elements of the aggregate structure.

The flow against the interior viscosity may be described as follows.

Let the bulk viscosity of the solution be η_s and the interior viscosity η_i. Let us isolate a pair of molecules of chain length L, lying one upon the other, but in different streamline levels, with a velocity gradient of $\partial V/\partial r$. Let the distance between the molecules be δ. Then the difference in the velocity of the solution in the two levels will be $(\partial V/\partial r)\delta$. The shear stress ($F_1$) of the surrounding liquid will be:

$$F_1 = \eta_s \frac{\partial V}{\partial r} S$$

where S is the surface of molecular contact.

On the other hand, the force developed between the two neighboring molecules (F_2) is

$$F_2 = \eta_i \frac{V_m}{\delta} S$$

where V_m is the relative velocity of the molecules. At constant flow velocity, the forces F_1 and F_2 become equal and

$$V_m = \frac{\eta_s}{\eta_i} \delta \frac{\partial V}{\partial r}$$

It is assumed that the structure is destroyed when the pair of molecules considered have moved, relative to each other, all along their length and have separated entirely.

If the mean molecular length is L, the time (T) necessary for the process is

$$T = \frac{L}{V_m} = \frac{\eta_i}{\eta_s} \cdot \frac{L}{\delta} \cdot \frac{I}{\left(\frac{\partial V}{\partial r}\right)}$$

An inspection of Figure 2 shows that the decrease of the pressure with time is, indeed, linear. This can be taken as an indication of a constant viscous flow in the structure.

It might be expected that η_i, η_s, $\frac{L}{\delta}$ are constant; hence $T(\partial V/\partial r)$ should be constant. This is borne out by the experiment. (For a degree of polymerization of 10,000, η_i is of the order of magnitude of 10 poise).

The authors are greatly indebted to Professor M. Reiner for his constant interest in this investigation and his helpful suggestions.

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THE DIRECT REINFORCEMENT OF RUBBER IN LATEX. II. SYNTHETIC RESINS FORMED IN SITU BY THE ADDITION TO LATEX OF THE STARTING MATERIALS OF THEIR RESINIFICATION *

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INTRODUCTION

Experiments previously described[1] led us to investigate what would be the result of incorporating in latex the intermediate products of resinification. With this objective, we studied the behavior of many types of resins. We immediately discovered that only a few resins met the conditions, which require compatability of the resins with mixtures of heat-sensitive latex[2], and we ultimately limited ourselves to urea-formaldehyde and phenol-formaldehyde resins.

When partially condensed resins are used, gelation of a heat-sensitive latex mixture can be controlled fairly well. In fact, because the aldehyde is rapidly destabilized by combining with phenol or urea at the moment of introduction of the resin, the ammonia in the latex does not tend to react, but continues to play its role of preservative and is, therefore, still in a position to contribute to the formation of complex zinc-ammonium ions.

We shall see that the aminoplasts do not give complete satisfaction. On the contrary, phenolplastic resins give vulcanizates of great promise in that they impart a notable reinforcing effect, depending on the nature, state, and proportion of resin. It was with formaldehyde and resorcinol that the most interesting results were obtained. In addition, a detailed study of the conditions of formation of this resin was indispensable to successfully carrying out the tests. We shall give only an outline here[3], before passing on to an investigation of the behavior of such resins in latex mixtures and of the properties of the vulcanizates obtained, and shall reproduce or amplify certain results previously published by Le Bras and ourselves[4].

UREA-FORMALDEHYDE RESINS

We have pointed out that the addition to latex mixtures which can be gelled and can be vulcanized of the elementary components or even of the first products of the condensation did not give conclusive results.

A resin of the same type in soluble form, prepared at the moment of use, behaved more favorably. Thus, for example, a mixture of urea and formaldehyde, catalyzed at a pH value of 7.2 and refluxed gently for 3 minutes, takes the form of a thick liquid of pH value 3, which is clear when warm, slightly turbid when cold, and automatically hardens on exposure to air. The resin is

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easily incorporated into the latex mixture; however, it then accelerates the heat sensitivity of the latex. For a content of this resin of 10 to 20 per cent, based on a 60 per cent latex, it was proved that the vulcanizates have a definite tendency to be reinforced. There is a pronounced stiffening and increase of tensile strength and resistance to tearing, while the percentage elongation remains substantially unaltered.

This reinforcement would certainly be higher if the resin could continue to be formed within the latex; however, we were not able to establish a compromise between the ammoniacal alkalinity necessary for stability and the heat sensitization of the degraded latex and the acidity favorable to the polymerization of aminoplasts.

CONCENTRATION OF THE RESORCINOL–FORMALDEHYDE SYSTEM IN AQUEOUS MEDIUM AT HIGH CONCENTRATIONS

The literature on phenoplasts is abundant, but rather poor, except concerning the particular case of resorcinol-formaldehyde condensation, for certain works of Dubrisay and Papault[5] and by Novotny[6]. It was, therefore, of interest to establish the conditions most favorable to the formation of the resin and under what conditions it gives the best results in latex.

CHOICE OF A REACTING SYSTEM

Preliminary tests led to the choice of the following base mix:

Resorcinol (pure crystallized)	4 parts	
Formaldehyde (30%)	4 parts	(E)
Sodium hydroxide (normal solution)	2 parts	

The mixture of reagents is at first a light and transparent liquid. The molecular F/R ratio of the components is close to 1. As for the catalyst, it was chosen for its great catalytic power in proportions of approximately 0.05 mole per mole of resorcinol; this accords well with the proportions ordinarily used in the phenoplast industry in general. Besides, the concentration of such a resin in dry solutions is of the order of 50 per cent and, therefore, it can be added to latex without diluting it excessively.

THERMAL NATURE OF THE CONDENSATION

Although there is a cooling effect when the reagents are mixed, the condensation reaction is essentially exothermic. After a rather brief induction period, the reaction becomes rather violent and progresses rapidly. If it is not controlled, it may lead to almost instantaneous resinification with evaporation of the water, or even to an explosion.

It is, therefore, advisable to resort to heat insulation. This has a decisive influence on the course of the heat phenomena. Either a water or an air thermostat can be employed, but the latter is not recommended, for the heat exchange is then small and can not arrest the heat wave which causes sudden gelation of the mixture.

RATE OF RESINIFICATION

The rate of resinification varies greatly, according to the conditions of the condensation.

The influence of temperature is in general well known; the condensation of a

resorcinol-formaldehyde resin in particular is proportionately more rapid as the temperature is increased[7]. However, the relation between the rate of resinification and temperature, is not so well known; it is expressed by an exponential law.

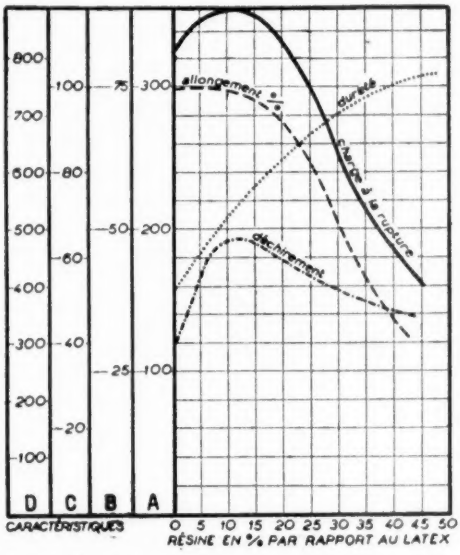

FIG. 1.—Mechanical properties of latex mixtures containing urea-formaldehyde resin. A Tensile strength (kg. per sq. cm.); B Hardness (Shore instrument); C Resistance to tearing (kg. per cm. by ASTM method); D Elongation at rupture (percentage). The abscissa indicated as "Résine en % par rapport au latex" indicates the resin content expressed in terms of percentage based on the latex. With reference to the curves, "charge à la rupture" is tensile strength, "allongement" is elongation at rupture, "déchirement" is resistance to tearing.

The influence of the pH value is manifest in various ways. In the study of this factor, it is necessary to consider:

(1) the pH value in solution of the various reagents, especially formaldehyde and resorcinol;
(2) the chemical action of the catalysts on the reagents;
(3) the pH value resulting from the addition of catalysts having an alkaline or acid reaction to the resorcinol-formaldehyde system.

Investigation of the relation between the rate of resinification and the pH value of the reaction system when the resorcinol and formaldehyde are in a molecular ratio close to unity enables us to confirm certain previous results[8] and throws a new light on the process of this condensation reaction. In fact the rate of gelation (see Figure 2) is found:

(1) to decrease up to a pH value of 3–4 when the pH value increases;
(2) to reach a minimum at pH 3–4 and then increase up to pH 7.5;
(3) to show a maximum at about pH 7.5 and then decrease at higher pH values.

In determining the coordinates of certain points by logarithmic transposition of the time-pH curve, we were able to show a duality of the phenomenon of

resorcinol-formaldehyde condensation as a function of the pH value. This process can be applied to all resorcinol-formaldehyde resins at any stage of resinification, independently of the temperature, concentration, and molecular ratio of the original components.

The simultaneous influences of temperature and of pH value are cumulative, and their study makes possible the construction of a whole series of useful graphs.

The influence of the concentration is also characterized by a continuous

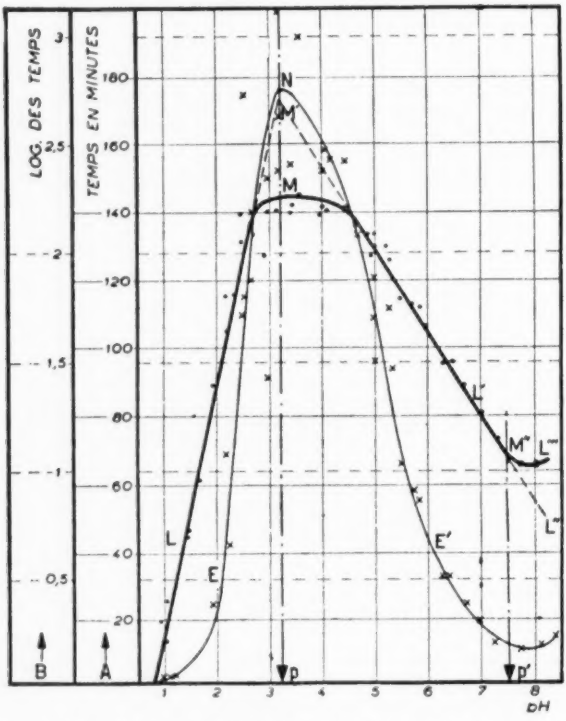

FIG. 2.—Influence of the pH value on gelation (in one step) of a mixture of resorcinol 4, formaldehyde 4, and catalyst, variable. The abscissa represents the pH values; the ordinate, the logarithm of time (where indicated as "log. des temps) and time in minutes (where indicated as "temps en minutes").

change: the greater the dilution, the more the rate of gelation of the resin is reduced.

The influence of the molecular ratio of the reagents is specific. The rate of gelation increases with the molecular ratio F/R and reaches a maximum when this ratio becomes equal to 3 (see Figure 3). There is a direct correlation between this ratio and the maximum number of alcoholic CH_2OH groups which can be fixed by each molecule of resorcinol. Another interesting point is the existence of a range of molecular ratios F/R close to 0.6 where gelation does not take place.

The influence of modifiers of the rate of resinification is relative. Most of the standard retarders, such as phenol and xylenols, have rather a diluting

action; methyl alcohol on the other hand, is a definite retarding agent, whereas ammonia and hexamethylenetetramine have an appreciable accelerating action.

PROPERTIES

The conditions of preparation determine the properties, which also depend on the degree of condensation. The usable resins have a slightly aldehydic odor, are in liquid form of about 50 per cent concentration, and have a slightly

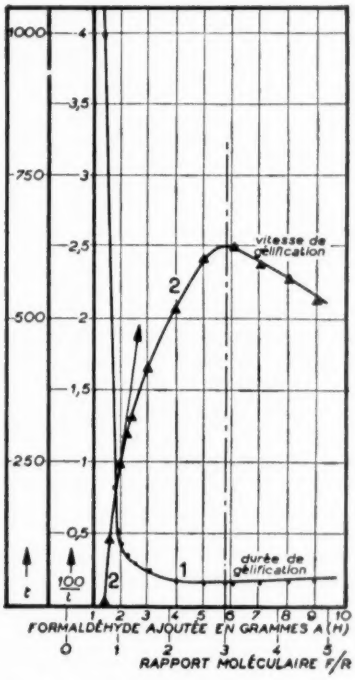

FIG. 3.—Influence of the molecular ratio F/R on the rate of gelation of a mixture of resorcinol 2; formaldehyde, variable; normal sodium hydroxide 1; distilled water to constant volume: 12 cc. (H). The French legend on curve 1 is the time of gelation; on curve 2 is the rate of gelation. The upper legend of the abscissa represents the amount of formaldehyde added in grams. A (H); the lower legend represents the molecular ratio F/R.

alkaline pH value. They can be diluted with water containing an alkali and are miscible with latex, but they precipitate in an acid medium. Their surface tension is lower than that of water. Nevertheless they are rather unstable, for they continue to polycondense uninterruptedly. This can be prevented to some extent either by dilution or by lowering the pH value, or by doing both.

BEHAVIOR OF SOLUBLE RESORCINOL–FORMALDEHYDE RESINS IN LATEX MIXTURES

The results which follow show in particular the influence of different factors on the properties of the vulcanizates obtained[9].

OPERATING CONDITIONS

The resin is blended with the vulcanizing agents and the mixture is added to the latex. Gelation is carried out in a metal mold with zinc plates for 10 minutes at 70° C. After drying for two days in air, and then two days in an oven at 40° C, the product is vulcanized for 1 hour at 100° in an oven and standard test-specimens are died out to determine the mechanical properties.

Table 1

Tensile Strength of Vulcanized Rubber from Reinforced Latex as a Function of the Time of Condensation of the Resin

Time of condensation (min.)	Tensile strength of vulcanizates containing 10% resin (kg. per sq. cm.)
20	300
40	350
60	450
120	450
180	445
240	455
300	450
360	450
Control latex	330

The stability of the latex resin mixtures depends on various factors, the number, nature, effect, and importance of which will be the subject of further study; in the cases described in the present work, the average time of stability is 30 minutes. When removed from the mold the gels are harder than those of simple latex; furthermore fewer precautions are necessary for handling them.

CONDENSATION OF THE RESIN

A given resin of known composition (E) is without any reinforcing action unless it is added to the latex after a certain time of condensation (Table 1).

Table 2

Influence of the Conditions of Vulcanization on the Properties of Vulcanizates from Reinforced Latex

Influence of time of vulcanization at 100° C		Influence of temperature of vulcanization for 1 hour	
Time (min.)	Tensile strength (kg. per sq. cm.)	Temperature (° C)	Tensile strength (kg. per sq. cm.)
30	425	70	360
40	415	80	450
50	460	90	475
60	475	100	475
70	485	110	465
80	480	120	325
90	475	130	175
100	470	140	150
110	450	150	150
120	440		
130	440		
150	445		

The optimum period of condensation is closely related to the rate of fixation of the formaldehyde on the resorcinol, but practically, for technical reasons, it is better to stop condensation after an hour, at the beginning of the plateau of maximum properties.

CONDITIONS OF VULCANIZATION

The vulcanization of a control latex mixture containing no resin is normally carried out in an oven at 100° C for an hour. Addition of the resin does not disturb the vulcanizing system, and, with a content of 10 per cent (based on 60 per cent latex), rather extensive plateaus are found under the same conditions of vulcanization (see Table 2).

PROPORTIONS OF CATALYST

The catalyst governs the nature and molecular size of the different components of the resin so, as was to be expected, it was found that sodium hydroxide in the reaction medium influences to a high degree the ultimate reinforcement (see Table 3).

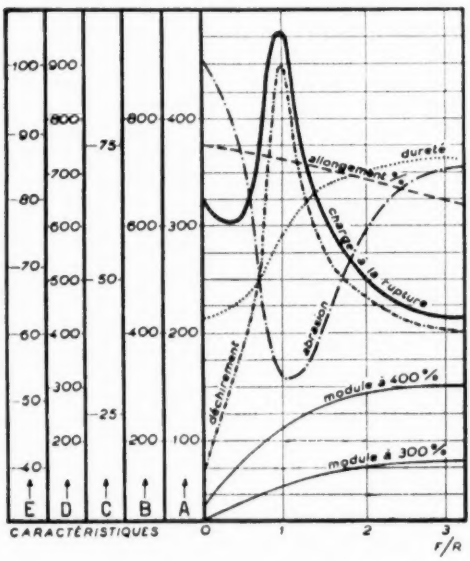

FIG. 4.—Influence of the molecular ratio F/R on the properties of latex mixtures containing 10 per cent of resorcinol-formaldehyde resin.

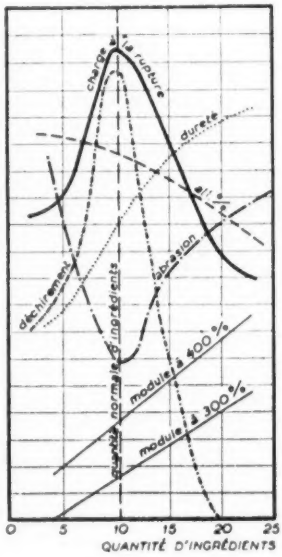

FIG. 5.—Influence of the proportion of vulcanizing ingredients on the properties of latex mixtures containing 10 per cent of resorcinol-formaldehyde resin.

FIGS. 4 and 5.—On the ordinate, A represents the tensile strength, modulus at 300 per cent elongation, and modulus at 400 per cent elongation, respectively; B the percentage elongation at rupture; C the hardness (Shore); D the abrasion resistance (cc./CV by the Grasselli method), and E the resistance to tearing kg./cm. by the A.S.T.M. method).

MOLECULAR RATIO OF THE COMPONENTS

The molecular ratio of the components is of prime importance. Addition to the control latex mixture of a given amount of the resin mixture prepared

TABLE 3

INFLUENCE OF CONCENTRATION OF SODIUM HYDROXIDE ON THE PROPERTIES OF VULCANIZATES FROM REINFORCED LATEX

Molecular ratio NaOH/resorcinol in (E)	Tensile strength (kg. per sq. cm.)
0.	200
0.01	330
0.02	400
0.03	425
0.04	435
0.05	460
0.06	475
0.08	480
0.10	455
0.12	390

under the same conditions, so that this ratio is the only variable, a well-defined point of reinforcement maximum is observed. The properties of these vulcanizates differ. First of all, both the hardness and the modulus increase with increase in the molecular ratio F/R, whereas the elongation at rupture changes very little. Furthermore the tensile strength, resistance to tearing, and abrasion resistance reach very high maximum values (see Figure 4).

To put it briefly, the vulcanizate obtained with 10 per cent resin, with molecular ratio, F/R, equal to 1, has remarkable properties, which are definitely superior to those now known among rubber products in general.

Table 4 shows the important mechanical properties of such a vulcanizate, and gives comparative values for a control latex mixture and a mixture prepared from masticated rubber of the standard tire-tread type containing carbon black as the reinforcing agent.

TABLE 4

COMPARISON OF VULCANIZATES FROM REINFORCED LATEX, ORDINARY LATEX, AND MASTICATED RUBBER

	Reinforced latex	Control latex	Rubber-carbon black
Tensile strength (kg. per sq. cm.)	460	330	310
Modulus at 300% (kg. per sq. cm.)	60	15	100
Elongation at rupture (%)	750	750	500
Resistance to abrasion (Grasselli, cc./CV/hr.)	300	600	350
Resistance to tearing (A.S.T.M., kg. per cm.)	100	50	90
Density	0.95	0.93	1.2
Hardness (Shore)	62	42	68

This superiority extends to the resilience and resistance to repeated flexing, which are comparable to those of the control latex mixture. The dielectric properties and heat conductivity surpass those of the masticated mixture reinforced with carbon black, and this superiority holds true also of resistance to flexing while hot in a Goodrich flexometer and to hysteresis after applied stress. Another advantage is the low specific gravity (at least 25 per cent), which is quite notable.

PROPORTION OF RESIN

There is likewise an optimum proportion of resin, viz., 10 per cent. Above this proportion, the reinforcement is relatively slight, although its effect on resistance to swelling in solvents is of interest.

THE VULCANIZING SYSTEM

Sulfur, zinc oxide, and the accelerator, zinc diethyldithiocarbamate, are indispensable. However, notable variations of the optimum proportion of each of these ingredients in the mixture have no undesirable influence on vulcanization and reinforcement, except perhaps for zinc oxide, which tends to stiffen the mixtures.

On the other hand, if the proportion of the ingredients ordinarily required for vulcanization is altered, in proportion, and in the same sense, then considerable changes in properties are observed. Up to the usual proportion (see Figure 5) the dispersed ingredients act as a reinforcing system; above this proportion they act as an inert filler.

AGING OF THE VULCANIZATES

Like ordinary latex, reinforced latex mixtures have a cream color at the moment of gelation, but, as drying continues, they undergo color changes which are very characteristic. A gradual green shade, turning bluish green, is observed, and this in turn changes to black after complete drying and vulcanization. This peculiarity, in addition to the properties of the mixtures, gives vulcanized reinforced latex the appearance of a masticated mixture reinforced with carbon black. This phenomenon is the result of the oxidation of resorcinol in the presence of ammonia, forming an insoluble dye of the azine type.

The aging of reinforced vulcanizates is quite satisfactory; it is superior even without the addition of an antioxygenic agent or of a deactivating agent to that of the control latex mixture, which is considered particularly resistant (see Table 5). Even after 40 days of aging at 70° C, its tensile strength is still superior to that of the vulcanized control latex which has not been aged.

THEORETICAL CONSIDERATIONS OF THE REINFORCEMENT OF LATEX BY RESORCINOL-FORMALDEHYDE RESIN

If we take into account that the numerous investigations on the reinforcement of rubber by carbon blacks have not yet, even after twenty-five years, led to any entirely satisfactory explanation of the phenomenon, it is reasonable to assume that the exact process of reinforcement by resorcinol-formaldehyde resins will still require many and long researches.

However, even now an explanation may be forthcoming, which is based on comparisons between certain experimental observations and earlier investigations concerned directly and indirectly with rubber.

CHEMICAL NATURE OF THE REINFORCING RESIN

When formaldehyde reacts with resorcinol, various compounds are formed, which by subsequent condensations, lead to different components of the final resin which are distinguished by their form and molecular size. The chemistry of resorcinol-formaldehyde resins is still not understood, but certain assumptions regarding their structure can be made, provided that one essential condition is met, namely that the molecular ratio, F/R, is unity, which, as we have seen gives the maximum reinforcement.

In this case the initial reaction products (see Figure 6) are phenol-alcohols probably containing predominantly 1,3-dihydroxy-2-methylolbenzene (I). The latter, in the first stages of condensation, forms, with resorcinol, tetra-

hydroxydiphenyl methanes (II) (six isomers) and with formadlehyde or with itself, it gives monomethyloltetrahydroxydiphenyl methanes (III) (eighteen isomers). The number of isomers increases rapidly with the number of nuclei (there can be cyclic compounds), and to isolate an intermediate product is practically impossible. As Champetier[10] wrote, in a more general case, we can assume that "the combination of phenol and formaldehyde can take place either in *o*- or in *p*-position. These two types of reaction proceed irregularly

TABLE 5

COMPARISON OF THE AGING OF VULCANIZATES FROM REINFORCED LATEX AND FROM ORDINARY LATEX

	Days at 70° C	0	2	5	10	20	30	40
Reinforced latex	Tensile strength (kg. per sq. cm.)	470	460	450	420	400	370	340
	Loss (%)	–	2	4	10	15	21	28
Control latex	Tensile strength (kg. per sq. cm.)	320	335	325	295	235	190	170
	Loss (%)	–	–	–	8	26	40	47

and a non-periodic disposition of the constituent elements results. On the other hand, it seems probable that the play of free rotation causes, before the final stage of condensation, continual changes of direction which, during the growth of the macromolecule, do not allow structural periodicities to appear"; consequently there is a preponderance of amorphous state resulting from the "gel-precipitation"[11] of the different compounds present. The colloidal properties of these latter suggest the presence of molecules containing 4 to 10 nuclei[12], in the simplest case 3 poly(2,6-dihydroxybenzyl)-2,6-dihydroxybenzylol (IV), with or without oxygen bridges, ether oxide bridges, or methylenic bridges resulting from intermolecular or intramolecular reactions. In any case, the molecule contains only one free primary alcoholic group.

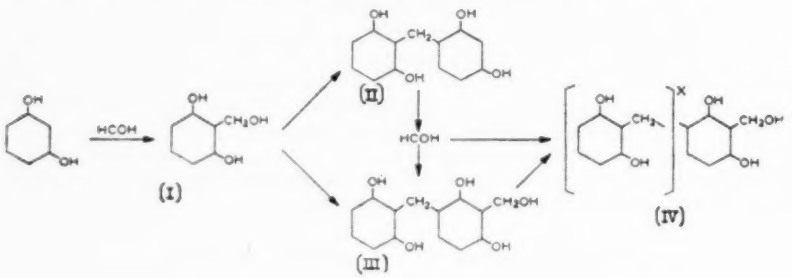

FIG. 6.

REACTIVITY OF PHENOL RESINS WITH RUBBER

Although there are no data on the possible compounds which resorcinol-formaldehyde resins may form with rubber, investigations nevertheless have been made in the field of phenoplasts in general, and several theories have been advanced.

Wildschut[13] succeeded in vulcanizing rubber with the sole aid of so-called "active phenol resins" soluble in benzene, but not with Novolacs and ordinary

resols, which are soluble in alcohol, including plasticized resols such as Durophen-219W, Albertol-142R[14], and Bakelite Resin-3360[15]. The mixtures contained 40 per cent of resin, based on the rubber, and were in most cases vulcanized for 2 hours at 160° C in a press. There are two theories which may explain this vulcanization. The chromane theory of Hultzsch[16] has been already applied by Greth[17] to resols and fat oils. This theory involves the idea of the formation of chromatic rings.

Considered insufficient, it has been replaced by the quinone *o*-methylene theory of van der Meer[18], which has been confirmed experimentally.

Both these theories imply a process characterized in general by a reaction between a resol and two linkages in the rubber molecule. Since the combining power of the resol is limited to the primary alcoholic function, it follows that vulcanization by the resol is impossible, unless the molecule bears two primary alcoholic groups. Furthermore, it is necessary that the position of the latter be favorable. These conditions are fulfilled by the "active resins" and, in general, by phenyl-dialcohols.

REINFORCED LATEX

The theory of the vulcanization of rubber by resorcinol-formaldehyde resins either by the chromanic process or by the *p*-methylene quinone process must be given up for the following reasons.

These two processes, as has been said, imply the presence of a primary alcohol group —CH_2OH— at each end of the intermediary molecules of the formaldehyde-resorcinol condensation. Now, under the conditions most favorable to reinforcement, the first molecular ratio, F/R, leaves very few possibilities for the formation of compounds containing two alcoholic groups and located in these positions. Moreover, some resorcinol would remain which had not reacted with the formaldehyde. However, if any resorcinol actually does remain, it is merely a trace.

Furthermore, if we assume that a certain proportion of intermediate molecules with two terminal primary alcoholic groups had been formed, these molecules would probably have to be made up of a dozen or more benzene nuclei. According to van der Meer[18], however, the vulcanizing power of phenyl dialcohols decreases rapidly with increase in molecular weight. It is reduced by 3/4 from *p*-cresol dialcohol to 2,2′-dihydroxy-5,3′-dimethylol-5,5′-dimethyl diphenylmethane.

In all cases of maximum reinforcement, the concentration of formaldehyde-resorcinol, expressed on a dry basis, is of the order of 8 per cent of the dry rubber, against 40 per cent in the experiments of Wildschut, the vulcanization time one hour against several hours, and the temperature 100° C, against 150° to 200° C. Besides this, even under such conditions, it has been found that the resin is incapable of vulcanizing the latex mixture; the mass obtained swells and is dispersed in the benzene, leaving a resinous skeleton.

Furthermore, simple combination of the resin with the rubber hydrocarbon would certainly not seem to take place. The various intermediate molecules, which in general would contain only one free methylol group, would have a greater tendency, during post-condensation, to combine with each other than with the rubber.

Although x-ray diagrams show the rapid appearance, during stretching, of the phenomenon of crystallization of the rubber hydrocarbon in vulcanized reinforced latex[19], swelling tests show conclusively, in accord with the theory

of Gee[20], that there has been no change in the rubber (Figure 7). Without reacting at all with the rubber, the resin is only polycondensed within the mixture, under a form which does not swell and, therefore, with reduction in the maximum swelling.

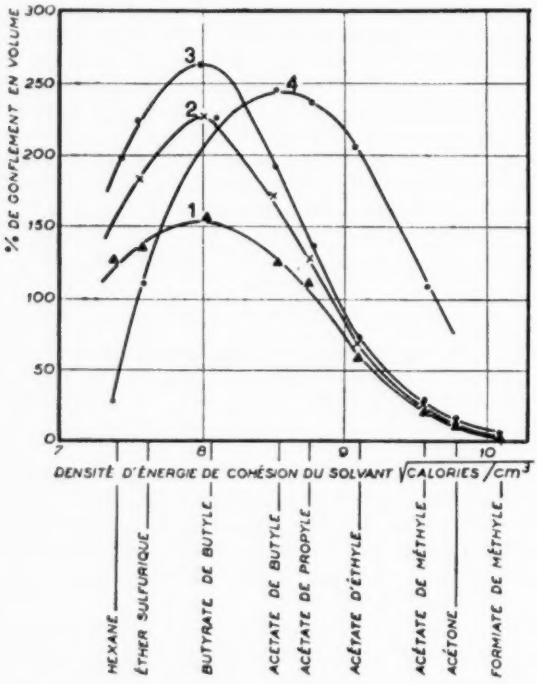

FIG. 7.—Curves of Gee. 1. Reinforced latex containing 10 per cent of resorcinol-formaldehyde resin; F/R ratio 1. 2. Control sample of pure latex. 3. Pure-gum mixture. 4. Perbunan-18 mixture. The ordinate represents swelling in percentage by volume. The abscissa represents the density of the energy of cohesion of the solvent in $\sqrt{\text{calories per cc}}$. Nine compounds indicated on the abscissa are (from left to right) hexane, ethyl ether, butyl butyrate, butyl acetate, propyl acetate, ethyl acetate, methyl acetate acetone, and methyl formate, respectively.

One can picture then, in the light of these ideas and these facts, that under normal conditions the resin is not combined, but is dispersed. It would seem that we are dealing with a specific reinforcing agent, which is extremely finely divided, and that this division is facilitated (1) by the resin having a colloidal character and being perfectly miscible with the latex and (2) by the microscopic canals present in the latex gels.

However, it is hardly possible at the present time to make any hypothesis about the mechanism which is responsible for the reinforcement observed.

CONCLUSIONS

This study makes it clear that fillers ordinarily used in the rubber industry impair the properties of latex mixtures. On the other hand, certain organic fillers, in solution and in dispersion, which are susceptible to certain chemical

modifications within the latex mixtures in which they have been incorporated, and with which they are compatible, have a favorable effect.

Consequently, by introducing into a latex mixture which can be gelled and vulcanized a suitable quantity of formaldehyde-resorcinol resin, in particular a soluble formaldehyde-resorcinol resin, prepared in slightly alkaline pH medium under certain carefully defined conditions, it was possible:

(1) for the first time to obtain reinforced articles directly from natural rubber latex, and

(2) to obtain an ensemble of properties superior to those at present known in the rubber world.

The reinforcement which has been found does not seem attributable to any chemical combination between rubber and resin, but rather to a specific structure of the resin-rubber mixture.

The way is now open to the direct use of latex in applications which were undreamed of previously. In fact, reinforced latex, possessing extremely high qualities, must be considered a new material, and it offers to technologists in the latex industry the opportunity to explore applications to heavy industry, such as belts, pneumatic tires, hose, and mechanical articles which must have high quality. Tests have already been undertaken in this direction[21], and they have given promising results and are being pursued actively. We may assume that, in the not too distant future, certain articles of reinforced latex will be manufactured on an industrial scale.

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A STUDY OF THE STAGE OF DISPERSION OF SYNTHETIC LATEXES BY THE INTENSITY OF LIGHT SCATTERING *

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In the polymerization of hydrocarbons in the form of aqueous emulsions, synthetic latexes are formed as ultramicroscopic dispersions of the polymer. The study of the state of dispersion of synthetic latexes as a function of the conditions of their formation and of the nature of the original substances (monomer, emulsifier, initiator, electrolytes in the aqueous phase) is interesting, first of all, as one way of explaining the topochemistry and mechanism of the polymerization process in emulsions. Furthermore, the results of such a study can prove useful in determining the properties of the latex itself, as well as those of the polymer dispersed in the latex.

The hypothesis that a predominant part of the emulsified polymer is formed in the hydrocarbon portion of the micelles of the emulsifier[1] explains a number of facts well, including the ultramicroscopic character of the state of dispersion of latexes. However, this process has been little investigated to date because of the complicating influence of various purely colloidal factors, as well as other factors, *e.g.*, the possibility of a similar course of the polymerization process in aqueous and nonaqueous media.

Yurzhenko and Mintz[2] were the first to establish that, during the process of polymerization of hydrocarbons in emulsion, a continuous growth of polymer particles takes place, although their number may remain practically constant, and equal to the number of micelles of emulsifier in the aqueous phase. During the polymerization of 1,3-butadiene, the type of emulsifier has an important influence on the volume of the polymer particles which are formed. These observations were confirmed in the latest works of two writers[3] and also in further studies on other substances made by the present authors.

The scientific literature, however, reveals no systematic study of the state of dispersion of synthetic latexes as a function of the conditions of their formation or of the nature of the initial substances. Even the problem itself has not been discussed. Available data on the state of dispersion refer only to individual samples of latex[4]. To fill this gap is the goal of the present investigation. The present paper contains data which were obtained by the authors and which are concerned chiefly with the application of the light-scattering method for the characterization of the state of dispersion of synthetic latexes.

The synthetic latexes were prepared in sealed ampoules having a graduated constriction in the middle for the observation of the rate of polymerization of the monomer from the contraction of volume. The initial substances (emulsifier, initiator, and monomer) were added to the ampoule in an atmosphere of

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nitrogen. The solution of emulsifier had first been treated with nitrogen. The sealed ampoules were put in a water thermostat at 50° C. Polymerization was effected by continuously rotating the ampoule (this was stopped only when the level of the emulsion was being measured) until the monomer was completely consumed. When this was not achieved, the remaining monomer was removed from the latex by centrifugation or evaporation.

The percentage of polymer in the latex was measured by the decrease of volume during polymerization, and also by the dry residue obtained after evaporation of the latex in a vacuum. These methods gave quite uniform results in most cases.

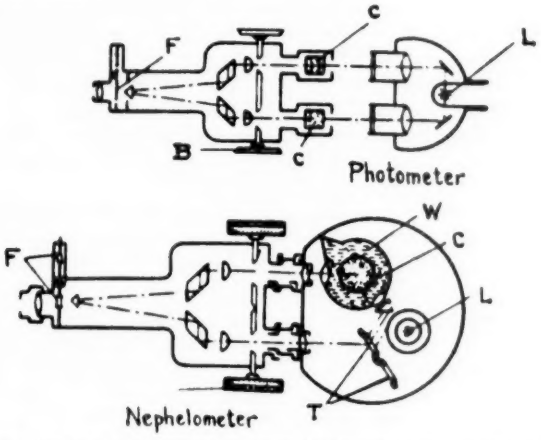

FIG. 1.—Diagram of apparatus for measuring the absorption and scattering of light

F—Light filter
B—Measuring drum
W—Water chamber
C—Cuvette with experimental liquid
L—Light source
T—Standard of turbidity

All the monomers with the exception of 1,3-butadiene were pure. In obtaining butadiene latexes, we used distilled butadiene containing 92.5 per cent pure butadiene. Sodium oleate was prepared by neutralizing oleic acid in absolute alcohol with sodium alcoholate, followed by recrystallization from absolute alcohol and drying in vacuo. Nekal (a sodium salt of dibutyl-α-naphthalenesulfonate) was crystallized three times from absolute alcohol in order to separate sodium sulfate. The pH value of the aqueous solution of emulsifier was regulated by adding sodium carbonate, an alkali or sulfuric acid.

DETERMINATION OF THE VOLUME OF THE POLYMER PARTICLES BY LIGHT SCATTERING

The light scattering method has found wide application, both for the measurement of the molecular weight of high polymers[5] and the micellar weight of colloidal electrolytes[6], and for the determination of the volume of larger particles in colloid systems[7]. We used the light-scattering method for characterizing the size of polymer particles in latexes, following in this case the rules established by Rayleigh and Debye. Some of the latexes were studied also by means of ultramicroscopy.

Measurement of the intensity of scattered light, I, and turbidity, τ, was made with a Pulfrich photometer with a nephelometric attachment (see Figure 1). For optimum visibility, a light filter was used with maximum transmission at about 5300° A. For determining the turbidity of the latexes studied, a Zeiss prism of milky glass with $\tau_0 = 0.0028$ cm.$^{-1}$ was used as a standard. The prism was placed in the same position as the experimental solution (the shapes of prism and cuvette were identical), and the intensity of the scattered light from the prism was compared with the intensity of light passed through a milky glass standard. The light scattered by the experimental solution was then also compared with the milky glass standard.

Before measuring the turbidity, the latexes were freed of monomer, filtered through a glass filter, and then diluted with a 1 per cent ammonia solution to prevent coagulation. Any turbidity caused by the pure diluting agents was slight and was subtracted from the turbidity of the diluted latex. The maximum dilution was 1:10^7.

The index of refraction of the aqueous medium, and also that of the latex, was measured with a refractometer, with an accuracy of 5 figures, *i.e.*, 4 decimal places at a constant temperature.

An explanation of the conditions of application of the known laws relating the size of scattering particles with the intensity of the scattered light (turbidity) must precede any application of the light-scattering method to synthetic latexes.

From the Rayleigh equation:

$$\frac{I}{I_0} = \frac{8\pi^3}{3} \cdot \left[3 \frac{n^{12} - n_2^2}{n^{12} + 2n_2^2} \right]^2 \cdot \frac{\nu v^2}{\lambda^4}$$

which can be more briefly written:

$$\frac{I}{I_0} = K \frac{cr^3}{d\lambda^4}$$

it follows that the value I/I_0, representing the turbidity τ, must be proportional to the concentration of polymer in the latex. Such a linear relation is observed, as the measurements show, only in a certain range of concentration. A linear relation between τ and λ^{-4}, following the Rayleigh's law was verified for synthetic latexes.

Besides Rayleigh's equation, Debye's equation[6] was also used:

$$\tau = \frac{32\pi^3}{3\lambda^4 N} \cdot \frac{cn_0^2 (\partial n/\partial c)^2}{\frac{\partial}{\partial c} (p/(RT))}$$

where N is the Avogadro number, n_0 the index of refraction of the solvent, c the concentration in grams per cc., $\partial n/\partial c$ is the concentration gradient of the refractive index, and $\partial p/\partial c$ is the concentration gradient of the osmotic pressure.

Bardwell and Sivertz[8], using this equation for synthetic latexes, obtained data approximately representing the size of particles found by other methods, such as electron microscopy, and adsorption titration.

The relation between the size of the particles and turbidity can be expressed more simply if the relation of osmotic pressure to concentration is calculated:

$$p = kT\left(\frac{c}{m} + A_1c^2 + A_2c^3 + \cdots\right),$$

where m is the mass of an independent particle, k is the Boltzmann constant equal to R/N, then:

$$\tau = \frac{32\pi^3}{3\lambda^4}\cdot\frac{n_0^2\,(\partial n/\partial c)^2 cm}{1 + 2A_1mc}$$

from which:

$$m = \frac{3\lambda^4}{32\pi^3}\cdot\frac{\tau/c}{n_0^2}\cdot\frac{1 + 2A_1mc}{(\partial n/dc)^2}$$

Introducing the concentration gradient of turbidity in place of τ/c and extrapolating τ/c to $c = 0$, we obtain for the radius of spherical particles:

$$r^3 = \frac{9\lambda^4}{128\pi^4 n_0^2 d}\cdot\frac{(\Delta\tau/\Delta c)_{c=0}}{(\Delta n/\Delta c)^2}$$

The determination of the concentration gradient of the refractive index of latexes is complicated by the fact that the averaging of the refractive index begins only after the formation of a certain amount of polymer in the diluted latex, when the distances between the particles of polymer become commensurate with the length of a light wave. This limiting concentration varies for different latexes. Thus, for polystyrene latex containing 20 per cent polymer, the influence of the latter begins to show only with a concentration above 0.01 per cent after dilution. For $\frac{\Delta n}{\Delta c}$ we took the angle of inclination of the straight line obtained. Bardwell and Sivertz[8] assumed this relation to be linear through the whole range down to $c = 0$.

EXPERIMENTAL DATA

RESULTS OF APPLICATION OF THE RAYLEIGH AND DEBYE EQUATIONS

Measurement of the turbidity of synthetic latexes in a wide range of polymer concentrations showed (see Figure 2) that the linear region of the τ-c relation extends only up to a certain concentration of polymer. With a further increase of concentration, the intensity of scattered light decreases after reaching a maximum.

Parallel measurement of light absorption by the same system leads to the conclusion that this loss of intensity of light scattering is related, on the one hand, to the absorption of scattered light in the latex itself, and, on the other hand, to weakening of the incident light passing through the latex. As is seen from Figure 3, in the region of small concentrations of polymer, absorption of light is negligible, and in this region the τ-c relation is strictly linear. Deviation from this relation is observed when the light absorption becomes great. Light absorption in latexes increases rapidly with further increase of polymer concentration.

The range within which the τ-c relation is linear for different latexes varies and depends to a large degree, as the experiments show, on the dispersion of

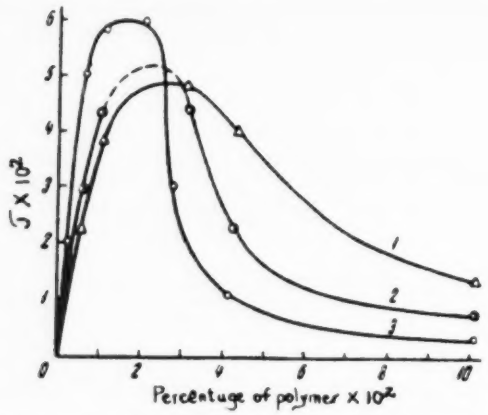

FIG. 2.—Relation of the intensity of scattered light in synthetic latexes to the concentration of polymer. Curve 1. 3% Nekal as emulsifier. Curve 2. 3% potassium laurate as emulsifier. Curve 3. 3% sodium oleate as emulsifier.

polymer in the latex. Thus, for polybutadiene latex, using as initiator diazoaminobenzene and as emulsifier sodium oleate, the τ-c relations is linear up to $c = 1 \times 10^{-3}$ grams of polymer in 100 cc. of solution, and for polystyrene is linear up to $c = 1 \times 10^{-2}$ grams per 100 cc.

Figure 4 shows the τ-c relation for polybutadiene latexes obtained at various conversions. The slopes of these curves represent the dispersion of polymer in the latexes.

Before calculating the size of the particles by Rayleigh's law, we investigated the light scattering of various latexes as a function of the wave length of the incident light. A typical photograph is shown in Figure 5 (polyisoprene

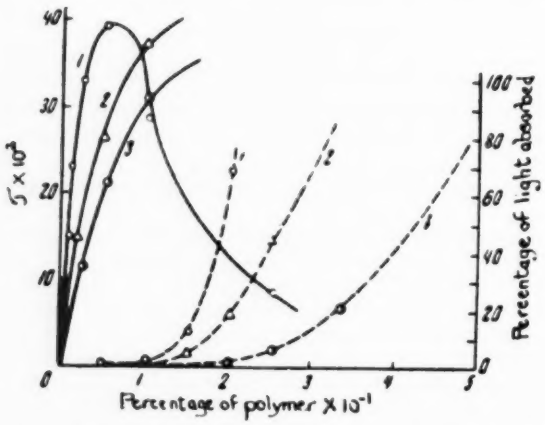

FIG. 3.—Scattering and absorption of light by synthetic (butadiene) latexes. Curve 1. 3% Nekal as emulsifier. Curve 2. 3% potassium laurate as emulsifier. Curve 3. 3% sodium oleate as emulsifier. The initiator was trimethylcarbinol hydroperoxide. The continuous curves indicate scattering; the broken curves indicate absorption.

latex). From these data, we see that the range within which the τ-c relation is linear extends farther (to the higher concentrations) as the wave length of the incident light increases. Furthermore, the intensity of the scattered light, as would be expected, increases with decrease of the wave length. The quantitative relation between τ and the wave length of the incident light is shown in Figure 6.

In Figure 6 we see that, at small concentrations of polymer in the latex, when $c = 0.55 - 1.1 \times 10^{-5}$ gram per cc., the intensity of the scattered light (turbidity) is proportional to λ^{-4}, and the corresponding points are satisfactorily close to a straight line. At higher polymer concentrations (2.7×10^{-5} gram per cc.) this linear relation ends.

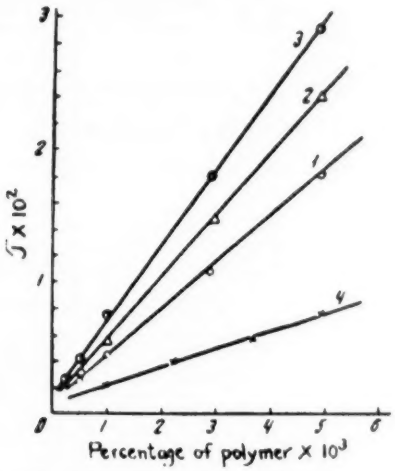

FIG. 4.—τ-c relation at lower concentrations. Curves 1, 2, and 3 for polybutadiene latex. Curve 4 for polystyrene latex. Polymer conversion: 1, 12%. 2, 18%. 3, 31%. 4, 25%.

Thus, from measurements of light scattering in synthetic latexes at various polymer concentrations and various wave lengths, it follows that Rayleigh's law can be applied to such systems only at suitable values of polymer concentration D; dilution of the original latex must be such that the linear character of the τ-c and τ-λ^{-4} relationships is maintained. These dilutions must be experimentally established. Assuming, however, a similar order of polymer dispersion in the synthetic latexes, we can estimate the permissible final concentration of polymer after dilution to be 1–1.5×10^{-3} per cent.

The table gives the sizes of the polymer particles of various synthetic latexes, calculated by means of the Rayleigh and Debye equations[9] and obtained by ultramicroscopic measurements.

From the data we see that the radius of the particles, found by various strictly comparable methods, varies to some extent, but the values can hardly be regarded as concordant, since latexes are polydispersed systems, and therefore the problem concerns the average radius. In each method, averaging is carried out differently. On the other hand, these discrepancies are also caused by inevitable experimental errors, such as incomplete counting of the number of particles in the ultramicroscope because of absorption of some of them on the

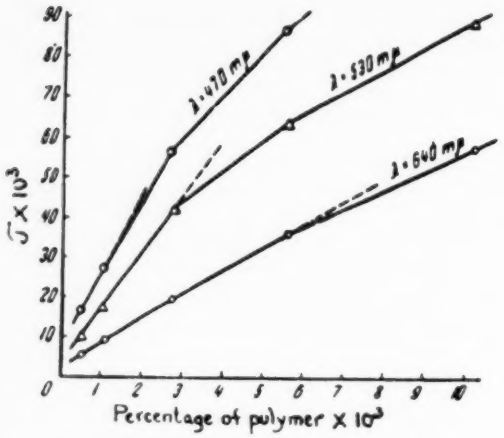

FIG. 5.—τ-c curves obtained for different wave lengths of incident light for polyisoprene latex.

TABLE 1

SIZE OF POLYMER PARTICLES OF VARIOUS SYNTHETIC LATEXES, FOUND BY LIGHT SCATTERING AND BY ULTRAMICROSCOPY

	Radius of polymer particles in mμ			
	Rayleigh's equation		Debye's equation	Ultramicroscopy
Latexes	c_{max}(%)	Radius		
Polybutadiene latex, containing 29% polymer	0.0005	58	42	87
Polybutadiene latex, prepared in Laboratory No. 1	0.001	38	28	50
Polybutadiene latex, prepared in Laboratory No. 2	0.0005	46	39	67
Polybutadiene latex, prepared in Laboratory No. 3	0.0005	60	52	85
Polystyrene latex No. 36, containing 20% polymer; 3% emulsifier (sodium oleate)	0.001	39	28	—

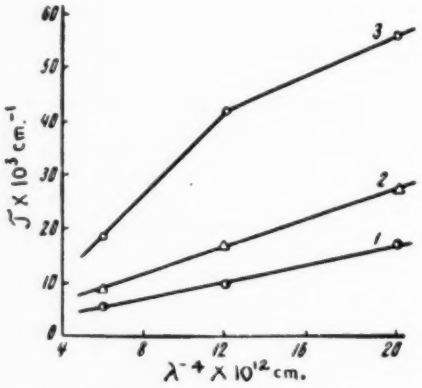

FIG. 6.—τ-λ⁴ relation for polyisoprene latex at various polymer concentrations. 1. 0.55 × 10⁻⁵. 2. 1.1 × 10⁻⁵. 3. 2.7 × 10⁻⁵.

walls of the cuvette or because of insufficient illumination, errors involved in the calculation of K in Rayleigh's equation, etc.

In any case, we come to the conclusion that various methods can be used in estimating the radius of polymer particles in latexes. If the light-scattering method is used, then the measurement of the intensity of the scattered light in synthetic latexes must be made at suitable dilution.

EFFECT OF CONVERSION ON THE SIZE OF THE POLYMER PARTICLES

This question is very interesting, because it concerns directly the mechanism of formation of polymer particles in emulsions. In fact, the number of particles in the polymerization process will vary, depending on whether the polymer particle is formed directly from droplets of monomer (emulsion polymerization), from a monomer truly dissolved in water, with ensuring stabilization of these particles by the emulsifier, or from a monomer in colloidal solution. Accumulation of the polymer in emulsion can be caused by an increase of the number of polymer particles once the forming polymer particle passes out of the zone of

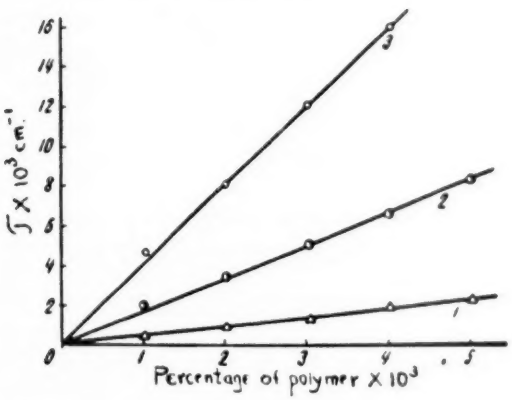

FIG. 7.—Light scattering by polybutadiene latexes of different conversions. 1. 6.2%. 2. 14.3%. 3. 29.2%.

reaction, as well as by an increase of their volume. During the polymerization of a monomer in colloidal solution, the number of particles of polymer can remain practically unchanged, and may correspond to the number of free micelles of emulsifier in the aqueous phase. The radius of the polymer particles will then be proportional to the cube root of the concentration of polymer in the aqueous phase. This relation was found earlier to be true of certain latexes[2]. Accumulation of the polymer in this case is caused largely by prolongation of polymerization of the polymer particles first formed in the micelles of emulsifier. Adding more monomer to the latex, we can cause a further growth of polymer particles as a result of their absorption of the monomer (swelling in the monomer) and polymerization of this monomer.

Figures 7 and 8 show the intensities of scattered light for butadiene latexes obtained at different conversions. From these data we see that, with increase of conversion, that is, as the polymer accumulates in the reaction system

(emulsion), the size of the polymer particles increases progressively; this leads to an increase of light scattered in these latexes. A similar picture was obtained for other emulsifiers and monomers.

For conversions of polymer in latexes of 6.2, 14.3, and 29.2 per cent, we have, accordingly, the following values of the average radii of the polymer particles: 62, 103, and 140 mμ, that is, the radius increases in the sequence 1:1.7:2.3. The value of $\sqrt[3]{c}$ here increases as follows: 1:1.4:1.8, that is, somewhat less than the radius. This may bear some relation to the partial agglomeration of the primary globules of polymer when the latex is stored. A greater divergence from the linear relation between r and $\sqrt[3]{c}$ was observed for small concentrations of polymer. For latexes with c = 14.3 and 29.2 per cent: $r_{14.3\%}:r_{29.2\%}$ = 1:1.35; a $\sqrt[3]{14.3}:\sqrt[3]{29.2}$ = 1:1.30, that is, a direct ratio between r and $\sqrt[3]{c}$ is

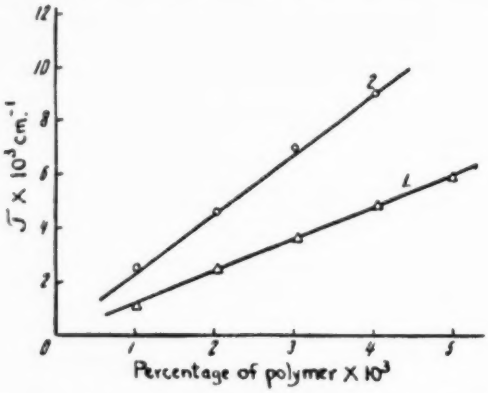

FIG. 8.—Light scattering by polybutadiene latexes of different conversions. 1. 3% polymer in final latex. 2. 4.5% polymer in final latex. Emulsifier was a 3% solution of Nekal.

maintained. Thus we come to the conclusion that the radius of the polymer particles in synthetic latexes increases with the accumulation of polymer in the latexes.

The increase of volume of polymer particles in latexes with an accumulation of polymer in the latex indicates that the polymerization process proceeds primarily in the aqueous phase of the emulsion through a stage of accumulation of polymer in the globules of the polymer which are formed at the beginning. Micelles of the emulsifier can also appear in place of these primary globules. Accumulation of polymer in the aqueous phase is chiefly caused, not by the increased number of polymer particles, but by their increased volume (growth). The number of polymer particles in latex during the process of emulsion polymerization changes little.

CONCLUSIONS

1. Light scattering in synthetic latexes of varying dilutions was studied as a function of the conditions under which the latexes were prepared. When the polymer concentration is increased, the intensity of light scattering reaches a maximum; this is related to the absorption of scattered light in the latex itself.

2. When the polymer concentration is less than 1×10^{-3} per cent, the

turbidity-concentration relation is linear. Calculation of the radius of polymer particles for this region of concentration by Rayleigh's equation gives results approximating those obtained by ultramicroscopy, but tending to be slightly lower. A similar picture is observed in the application of Debye's equation.

3. When the conversion is increased, the size of the latex particles increases. Accumulation of the polymer in the aqueous phase of the emulsion is largely the result of an increase of volume of the polymer particles, and not of their number.

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ABRASION PATTERN ON RUBBER *

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INTRODUCTION

When rubber is abraded on any of the customary abrasives, such as carborundum cloth, and its surface is examined at frequent intervals, it is found that at first scoring marks are produced, but, under suitable conditions which appear to be widely fulfilled, an array of nearly parallel ridges which run at right angles to the direction of abrasion forms on the abraded surface later on. This array of ridges will be called the *abrasion pattern*.

Similar ridges are found on the surface of motor-car tires, in particular on driving bands, where they are oriented at an angle to the direction of motion of the vehicle. The physical characteristics of the ridges on tires and of those produced in the laboratory are so similar that there can be no reasonable doubt that they have a similar origin.

The abrasion pattern tends to be very conspicuous on test-pieces used on the Akron abrasion machine and has most probably been noted by everyone concerned with this test, but only Blow and Garner[1] appear to have drawn attention to it. We have found no reference in the literature to the abrasion pattern on tires.

The purpose of this note is to describe qualitatively some properties of the abrasion pattern and to show that certain conclusions can be drawn from it as to the conditions under which abrasion of tires takes place on the road.

PROPERTIES OF THE ABRASION PATTERN

The properties of the abrasion pattern are, of course, best studied in the laboratory under controlled conditions. The apparatus employed for this purpose was very simple and consisted of an abrasion track about 2 feet long over which the abrasion sample was towed. The sample, $\frac{1}{8}$ inch thick and of 5 sq. cm. area, was mounted under a suitable carriage, and various normal loads could be produced by means of lead weights which were put on the carriage. The abrasive was silicon-carbide cloth (John Bull No. 150), and the abrasion velocity was 0.5 cm. per second. The track was cleaned after each run by hand with an air jet working under 2 atmospheres' pressure.

Three different vulcanizates of natural rubber were employed in the experiments, an unloaded soft gum vulcanizate and two compounds loaded, respectively, with 10 and 40 parts by weight of the channel black M.P.C. per 100 parts of rubber. Details of the formulas and curing conditions are given in the appendix. The rubber containing 40 parts of channel black is a typical tire-tread compound, and will be referred to as such.

Figure 1 shows the abrasion patterns produced under the same external conditions on the pure gum vulcanizate and the tire tread compound. The black marks and ink lines on the latter photograph should be ignored for the

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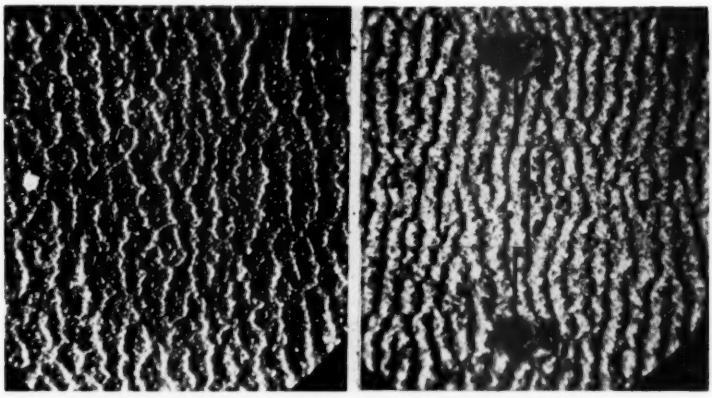
present. It will be seen that the two patterns are similar; the pure gum, being translucent, does not give such a contrasting picture as the opaque tire-tread compound. However, it has been found that, in general, soft compounds produce a more pronounced pattern than hard compounds.

On the same compound, the average spacing between the ridges increases with increasing normal load. This is illustrated by Figures 1 (*a*), 6 (*a*), and 5(*a*) showing abrasion patterns on the pure-gum vulcanizate produced at normal pressures of 0.4, 1.2 and 1.6 kg. per sq. cm., respectively.

Figure 1 (*b*) has been composed of two photographs of the abraded surface made at different stages of the abrasion experiment. There were two reference marks in the rubber surface, consisting of two small holes punched out of the surface and showing as the roughly circular marks on Figure I (*b*) which were subsequently joined on the prints by an ink line. The center part of Figure



(*a*) (*b*)

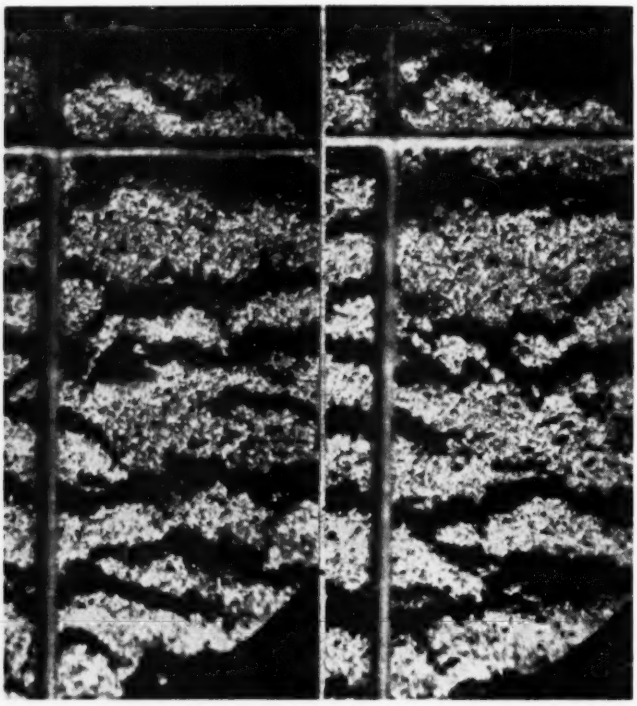
FIG. 1.—The abrasion pattern produced in the laboratory under 0.4 kg. per sq. cm. on: (*a*) pure gum vulcanizate; (*b*) tire tread compound. 20 ×. In (*a*) the abrasion is from left to right, and in (*b*) the abrasion is from right to left.

1 (*b*) is the photograph taken at the later stage, and it was pasted on the first photograph in such a position that the patterns matched as well as possible. It will be seen that the fit is remarkably good, although the thickness of rubber abraded between the two stages was about 2.5 times the height of the ridges. It will be seen also that the pattern has moved as a whole through a distance given by the displacement of the center part of the ink line, which, it is seen, is about 1.5 times the distance between the ridges. The direction of motion of the pattern is the same as that of the abrasive.

The effect is not confined to any particular sample nor to special conditions of abrasion. Figure 2 shows the abrasion pattern at two stages of the abrasion of a compound loaded with 10 parts of channel black. What appear to be heavy bars above the rubber surfaces are cross-wires made of 42 gage wire, with which the ridges could be located. The cross-wires were fixed to a frame which fitted tightly over the test-piece and could be placed back over it in the same position after each experiment. The abrasion was more severe here than in the previous case, but comparison between these two pictures shows that certain distinguishing features which can be discerned in Figure 2 (*a*) can be

traced again in Figure 2 (*b*) although in a distorted form, and that again the pattern as a whole has moved in the same direction as the abrasive.

The rate at which the pattern moves across the surface increases with the rate at which the surface is being abraded, that is to say, it depends on the normal load. An attempt has been made to obtain some quantitative data for this relation, but it should be realized that any figures obtained in this context give only the order of magnitude of the effect. The reason for this limited



(*a*) (*b*)

FIG. 2.—The abrasion pattern produced in the laboratory on the compound containing 10 parts of channel black. 1.6 kg. per sq. cm., 20 ×. Abrasion from top to bottom. See text.

accuracy is that the pattern does, after all, alter its configuration during the course of the abrasion experiment; when the abrasion is allowed to proceed too far between successive examinations of the surface in an attempt to increase the travel of the pattern and thus to raise the accuracy, it is found that the landmarks of the pattern which had been selected as reference points have become so altered that another source of experimental error arises out of the lack of definition.

The results with the tire-tread compound and with the sample containing 10 parts channel black may be summarized by stating that, on the average, the abrasion pattern traverses a distance which is 3 to 8 times the thickness of rubber abraded during the same time.

An interesting characteristic of the abrasion pattern is the profile of the

ridges. Figure 3 (*a*) shows a cross-section through the abraded surface of the pure-gum vulcanizate, the plane of the section being at right angles to the ridges. The section was cut with a freezing microtome. The cold stage was not cooled by the expansion of gaseous carbon dioxide but by a mixture of powdered solid carbon dioxide and alcohol. This technique provided automatic lubrication which did not attack the rubber. The ridges are asymmetrical with respect to the direction of abrasion, they have overhanging crests which lean forward against the direction of abrasion. In some cases, the tops of the ridges look very frayed.

(*a*)

(*c*)

FIG. 3.—Profile of abrasion pattern: (*a*) pure-gum vulcanizate, abraded in the laboratory under 1.6 kg. per sq. cm., 10 ×; (*b*) tire tread compound, abraded on the road. Abrasion from left to right. Horizontal magnification 60 ×; vertical magnification 85 ×.

The shape of the ridges and, in particular, their orientation with respect to the direction of abrasion, may at first appear surprising. It must, however, be remembered that during abrasion the ridges are all bent backwards and that material will be removed by abrasion from what is the underside of the ridges in the relaxed state which is, of course, shown by Figure 3 (*a*). The "undercutting" effect which is therefore brought about by abrasion makes it understandable why the pattern moves in the same direction as the abrasive. The practical importance of the peculiar profile of the abrasion pattern lies in the fact that inspection of the pattern under suitable conditions of illumination makes it possible to determine without ambiguity the direction of the abrasion to which the sample in question had been submitted.

ABRASION AND THE ABRASION PATTERN

The rate at which the surface of a soft rubber vulcanizate abrades is, in the first stages of the experiment, not constant, but depends on the length of the experiment, in the manner shown by curve (*a*) of Figure 4. Starting with a fresh sample, the initial rate of abrasion is low, but rises immediately and reaches a final value only after the sample has travelled over about 10 m. of the abrasive. During the same period the abrasion pattern develops until it is fully established at about the same time when the rate of abrasion becomes constant. Its appearance at this stage is shown by Figure 5 (*a*). In order to

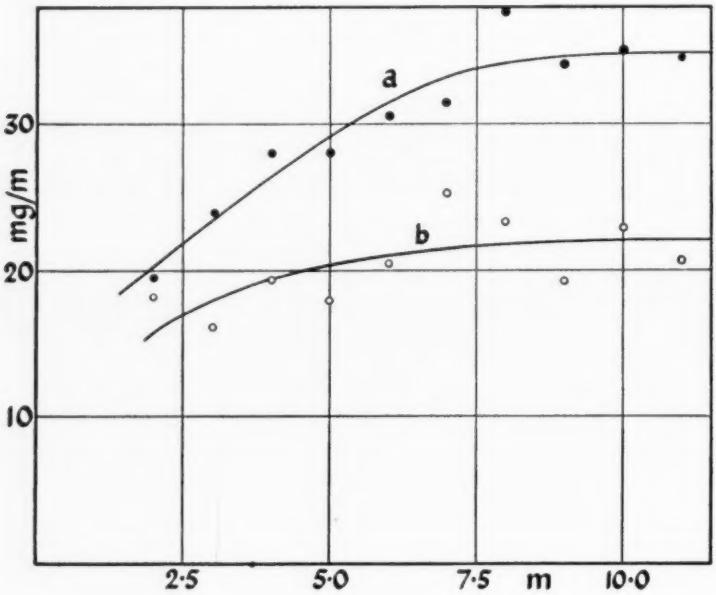


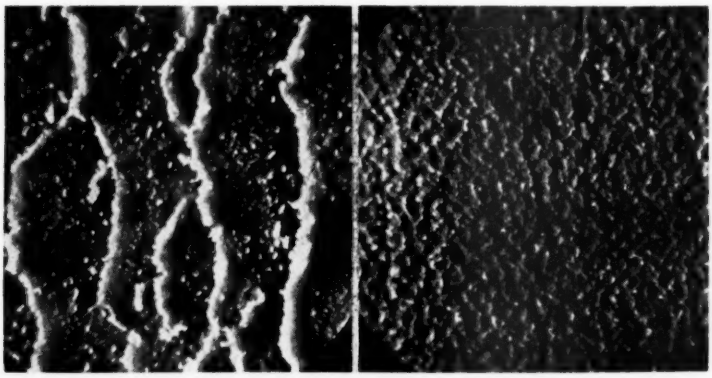
FIG. 4.—Dependence of the rate of abrasion on the length of the experiment, in mg. per 50 cm. travel; (*a*) sample abraded in constant direction; (*b*) sample turned 90° after each 50 cm.

ascertain whether the parallelism between these two processes, *i.e.*, increase of the rate of abrasion and development of the abrasion pattern, is a mere coincidence or not, the abrasion pattern was prevented from developing by the simple expedient of turning the sample periodically through 90° in its own plane. When this is done, the rate of abrasion depends on the length of the experiment, in the manner shown by curve (*b*) of Figure 4. At the very beginning, there is little difference between the rates of abrasion of the two samples, but later on the abrasion of the turned sample increases at a lower rate, and its final magnitude is lower, than that of the sample abraded in a constant direction. Also, the surface, as shown by Figure 5 (*b*), is much smoother.

There is no doubt that the abrasion pattern has an appreciable influence on the rate at which abrasion occurs, and it seems likely that the effect consists in adding a new source of abrasion to what may be called the ordinary abrasion,

that is to say, the abrasion which operates when for one reason or another no pattern develops. When describing the profile of the abrasion pattern of Figure 3 (*a*), attention was drawn to the ragged crests of some of the ridges. It appears that these crests were just on the point of being torn off, leaving the top of the ridge blunt like those of the other ridges on the same photograph. The removal of a crest is equivalent to prolonged abrasion of the ordinary kind which, as far as one can tell, proceeds on a much smaller scale and where only small amounts of rubber are removed at a time. The results shown in Figure 6, which will now be described, may also be referred to in this context.

The origin of the abrasion pattern is not yet fully understood, but it is most probably a consequence of the combination of high elasticity and high coefficient of friction which is characteristic of rubber. The influence of hardness has not been studied by us beyond making the observation, already referred to, that



(*a*) (*b*)

FIG. 5.—Abraded pure gum surfaces, 1.6 kg./cm.^{2}; (*a*) sample abraded in constant direction; (*b*) sample turned 90° after each 50 cm.

the pattern tends to be more developed on soft than on hard compounds. The influence of friction can be studied by varying the temperature because of the negative temperature coefficient of rubber friction. Figure 6 (*a*) shows a typical abrasion pattern produced at room temperature (15.5° C) and Figure 6 (*c*) the same surface after abrasion at 44° C. Not only is the abrasion pattern greatly reduced at the higher temperature, and therefore lower coefficient of friction, but the size of the abraded particles is also reduced as seen when comparing Figures 6 (*b*) and 6 (*d*). These photographs were secured by picking up the debris from the abrasion track with a microscope slide covered with semi-set cellulose varnish.

THE ABRASION PATTERN ON TIRES

The abrasion of tires was studied mainly with an experimental tire which had the standard tread seen in Figure 8, but circular plugs of eight experimental compounds were inserted in the driving bands around the circumference of the tire. The plugs were made in pairs, each compound being represented on both driving bands. One of the compounds was the pure-gum vulcanizate referred to earlier in this paper; other compounds contained varying amounts of channel

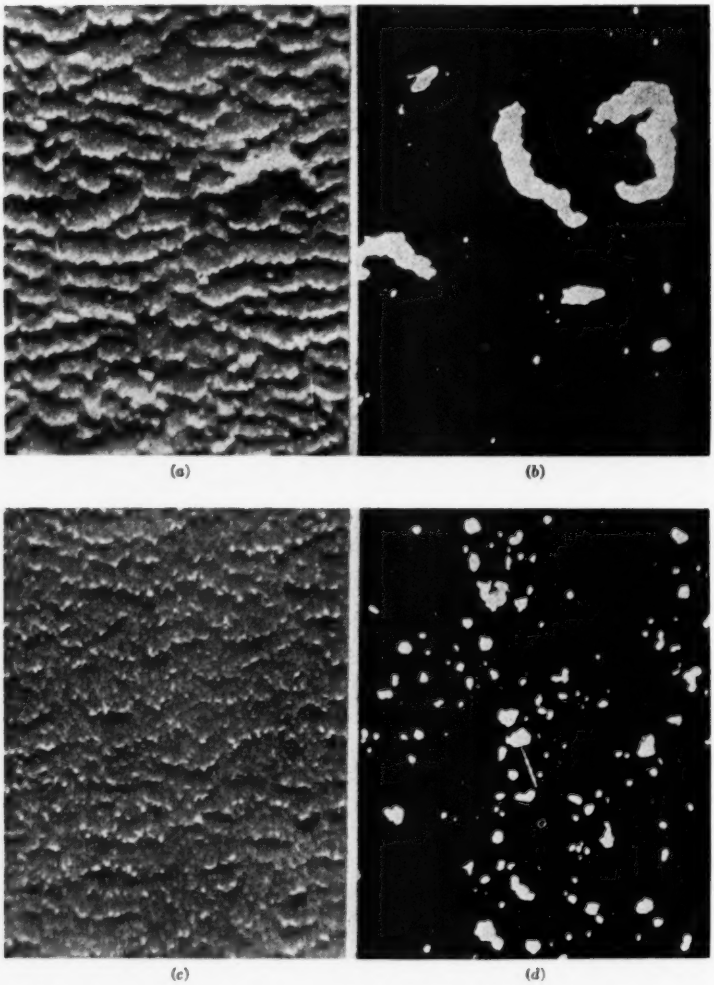


FIG. 6.—(a) Abrasion pattern on pure-gum vulcanizate at 15.5° C; (b) debris from abrasion at 15.5° C; (c) abrasion pattern at 44° C; (d) debris from abrasion at 44° C. 1.2 kg. per sq. cm., 20 ×.

black, the highest loading being 50 parts by weight, and one compound contained 100 parts of the nonreinforcing black P33. It was found that an abrasion pattern developed on all compounds to approximately the same degree, with the exception of the sample containing non-reinforcing thermatomic black, where the ridges were much more closely spaced than on any of the other samples.

Figure 7 (*a*) and (*b*) illustrate the actual abrasion of the pure-gum vulcanizate and the sample containing non-reinforcing black after about 7,000 miles road wear, during which the tire had been mounted on the rear off-side wheel of

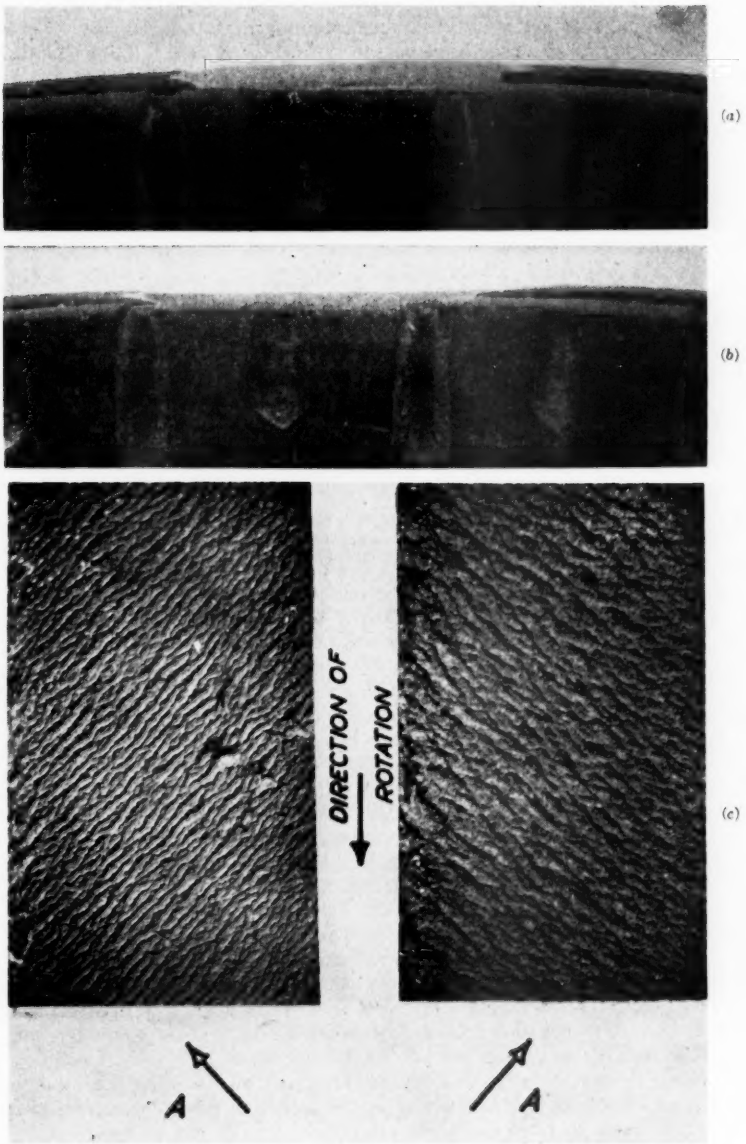


FIG. 7.—Results obtained with experimental tire: (a) abrasion of plug of pure-gum vulcanizate; (b) abrasion of plug of compound containing 100 parts of non-reinforcing P33 black; (c) abrasion patterns on tire tread compound (left) and pure-gum vulcanizate, 5 ×.

a delivery van. This test period covered just one year. It will be seen that the pure-gum compound had not been abraded more than the rest of the tire. Similarly, there was no visible difference between the other samples containing channel black and the main body of the tire. The sample containing non-reinforcing black, on the other hand, had been abraded considerably more than the tire tread, as is plainly shown by Figure 7 (*b*).

Figure 7 (*c*) shows the abrasion patterns on the pure-gum and on the tire tread compound. These two photographs were taken of samples situated in driving bands on opposite sides of the tire, and they were mounted in Figure 7 (*c*) in the same relative position as their originals on the tire. As mentioned in the Introduction, the ridges are inclined to the direction of motion of the vehicle, opening out in the direction of rotation. This orientation is not confined to the experimental tire, but has also been found on every tire that we have been able to examine, although the angle between the ridges on opposite sides of the tires may vary from case to case. Moreover, Figure 7 (*c*) shows that the patterns on the pure-gum vulcanizate and on the tire tread compound are very similar; the pattern on the pure gum is, however, somewhat rougher than on the tire tread compound, although the photograph does not show the difference very clearly.

By analogy with the results of laboratory abrasion, it can be deduced that abrasion of the tire occurred again at right angles to the ridges, that is to say, at an angle to the direction of motion. The actual direction can be ascertained from cross-sections through the patterns. Figure 3 (*b*) is a cross-section through the tire-tread sample of the tire, and the similarity between this photograph and Figure 3 (*a*) is so obvious that any remaining doubt about the origin of the pattern should be removed by it. The direction of abrasion as deduced from the cross-sections is indicated by the arrows marked A on Figure 7 (*c*).

This result is at first sight quite unexpected, and in order to understand it, it is necessary to discuss briefly the deformation of the tire when in contact with the road. A tire consists essentially of a fabric backing on which a rubber tread is built up. The cross-section of the tread is in the great majority of cases curved so that the surface of the undeformed tire has double curvature. When the tire touches the road and the tread is flattened, both principal radii of curvature increase and become infinite; the canvas backing, being flexible but not significantly extensible, acts as a neutral surface during this deformation, and it is easily seen that the tread, being on the convex side of the tire, becomes compressed. In other words, the tire tread shrinks when it comes into contact with the road, and its expands again when it leaves the road. This fact is demonstrated by Figure 8 which shows a replica of the deformed tire. This replica was made from a plaster cast prepared by making an impression of the mounted tire in plaster of Paris. It will be seen how the tread pattern curves in near the center of the area of contact and how, in particular, the gaps between the driving bands close in.

When the tire rolls, each point of the tread, on touching the road, moves relative to the road approximately in the direction towards the center of the instantaneous area of contact between tire and road; on leaving the road, each point moves away from the center of the contact area. The direction of these two distinct movements are, in the general case, different, but the existence of an abrasion pattern proves that abrasion, or at least most of the abrasion, occurs only during one of these movements. It is, in fact, immediately seen from the direction of the arrows on Figure 7 (*c*) that abrasion of the tire occurs prin-

cipally when the tire shrinks, that is to say, when the tire comes into contact with the road.

On the basis of the above argument one would expect that abrasion of the center of the tire was directed along the periphery of the tire, so that the ridges near the center should run across the tire. According to observation, this orientation of the ridges is indeed found sometimes, but in the majority of cases there is a preponderance of peripheral ridges, as for example shown by Figure 9,

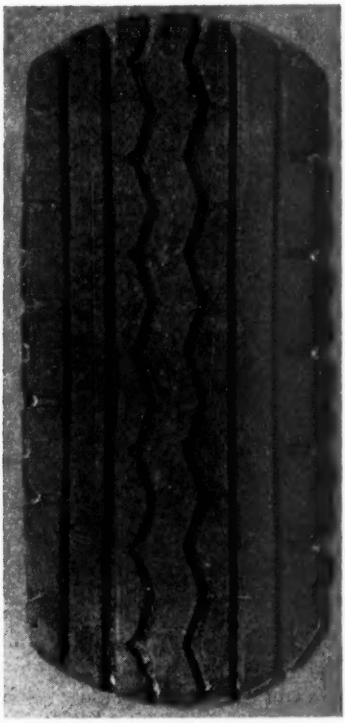


FIG. 8.—Deformation of tire by the road (replica).

which is a photograph of the center band of the experimental tire. These findings indicate that there is a certain amount of lateral motion of the tire, which is most probably caused by asymmetry of the tire itself or of its mounting.

The author has shown recently[2] that the difference in hardness between a pure-gum vulcanizate and a tire tread compound leads to a great qualitative difference in the type of surface damage which is produced on these two types of compound in an elementary kind of abrasion experiment, where the rubbers are scratched with a needle. In the same investigation it was shown also that large local strains are set up by the needle before local failure of the rubber occurs. Although the details of the mechanism of abrasion, either in the laboratory or on the road, are not known, it can be assumed that the conditions

encountered on the surface of the rubber where it is indented and otherwise deformed by the asperities of the abrasive or of the road are similar to those found in the needle scratching experiments. To judge from the results of this earlier investigation, one should have expected less developed abrasion patterns on hard than on soft compounds, and this has indeed been found to be so when the samples are abraded in the laboratory. It has been seen, however, that, according to Figure 7 (*a*) and, more particularly, Figure 7 (*c*), there is hardly any difference between the behavior of the pure-gum vulcanizate and the tire tread compound when exposed to abrasion by the road. The following explanation of this divergence of the results has suggested itself. During abrasion

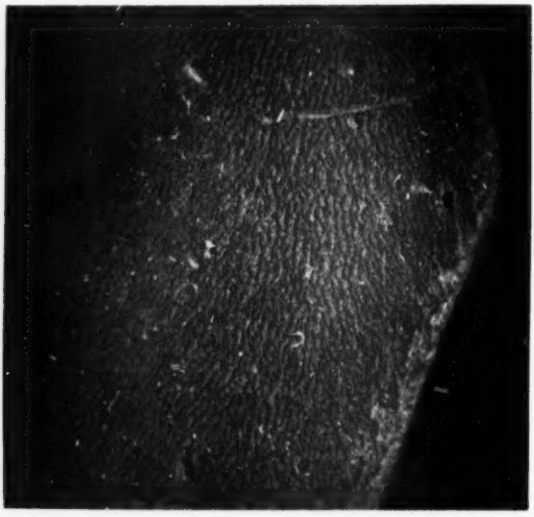


FIG. 9.—The abrasion pattern on the center band of the experimental tire, 5 ×.

on the road, large local strains are repeatedly produced, which eventually, but not immediately, lead to local failure.[2] The deformations discussed here should be sharply distinguished from the deformation of the tire as a whole which has been discussed above (see Figure 8). The deformation now being considered is on a much smaller scale, which is most probably confined to a surface layer less than 1 mm. thick. If the rubber in question is a compound loaded with channel black, such as a conventional tire tread stock, the repeated strain will reduce its hardness and so change its mechanical properties because of prestressing[3] that the difference between pure-gum vulcanizate and tire tread stock is largely obliterated. In short it is suggested that, as a consequence of repeated strains and of prestressing, there is on the tire a thin but constantly renewed top layer of material, with a much lower modulus than the bulk, the mechanical properties of which are not very different from those of a pure-gum vulcanizate, and the abrasive properties of which are also similar to those of a pure-gum vulcanizate.

The work reported here forms part of the research program undertaken by the Board of the British Rubber Producers' Research Association.

The experimental tire described in this paper was made by Henley's Tyre

and Rubber Co., Ltd., with plugs of experimental compounds provided by the Association. The author is glad to have this opportunity to thank Henley's Tyre and Rubber Co., Ltd., for this tire and to acknowledge gratefully the helpful cooperation of E. R. Thornley, their Chief Chemist.

SUMMARY

It has been observed that an array of nearly parallel ridges is often produced by abrasion on rubber surfaces. This array is called the "abrasion pattern." The ridges run at right angles to the direction of abrasion, and their profile is asymmetrical with respect to the direction of abrasion. Various properties of the abrasion pattern are described, and its use in the elucidation of the mode of abrasion of tires is discussed.

APPENDIX

The three experimental compounds used had the following composition in parts by weight.

Channel black (M.P.C.)	0	10.0	40.0
Rubber	100.0	100.0	100.0
Zinc oxide	5.0	5.0	5.0
Sulfur	2.5	2.5	2.5
Stearic acid	1.0	3.0	3.0
Santocure (accelerator)	0.6	0.6	0.6
Pine tar	0	0.5	2.5
Phenyl-β-naphthylamine (antioxidant)	1.0	1.0	1.0

They were cured for 50 minutes at a temperature of 142° C.

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[2] Schallamach, *J. Polymer Sci.* (in press).
[3] Mullins, *J. Rubber Research* **16**, 275 (1947); Buist, Lindsey, Naunton, Stafford, and Williams, *Ind. Eng. Chem.* **43**, 373 (1951).

CLASSIFYING BUTYL RUBBER WITH RESPECT TO MODULUS

A CHEMICAL METHOD *

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In the commercial production of Butyl rubber, the determination of modulus is of paramount importance. In addition to being the most important product specification, this curing characteristic is of primary concern to both the plant operator and the rubber processor. Since the inauguration of the synthetic rubber program, the modulus level has been determined by the stress-strain method of compounding, curing, and testing sample specimens of the finished polymer. In spite of numerous improvements[1], the stress-strain procedure is time-consuming and unreliable. Mill roll and press temperatures, humidity conditions, and chemicals are variables that require constant attention. The most serious shortcoming is the 24-hour time lag between the time of sampling and the reporting of a result. Consequently, stress-strain testing has been of little value in the control of Butyl rubber production.

For maximum product uniformity, a rapid reliable method for evaluating the effect of plant variables is required. This paper deals with the development of a chemical method for predicting modulus and its adoption for plant control purposes. This study has been based on the testing of the raw isoprene Butyl polymers listed in Table I, and its application to vulcanized stocks would require further work.

TABLE I

COMMERCIAL BUTYL GRADES

Feed stock[a]	Mooney range (ML8 minutes at 212° F)	40-Minute modulus range, (lb./sq. in.)	Commercial grades
B-1.0	40–50	—	PB.100, GRI-R-2
B-2.0	40–50	875–1125	PB.200, GRI-50
B-3.0	40–50	1125–1375	PB.300, GRI-YI15
B-2.5	70–80	1125–1375	PB.301, GRI-18
B-4.0	40–50	1325–1575	PB.400, GRI-Y-25

[a] B-1.0 represents a mixture of 99% isobutylene and 1% isoprene, B-2.0 represents a mixture of 98% isobutylene and 2% isoprene, etc.

Although all the Butyl polymers listed in Table I possess low unsaturation compared to natural rubber, it has been shown[2] that each possesses specific properties which depend on the amount of diolefin present. The properties chiefly affected are rate of vulcanization and the characteristics of the stress-strain curve. In developing a chemical method for predicting the rate of vulcanization, it has been necessary to improve the reproducibility of the method

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for determining the unsaturation content of Butyl rubber and to correlate the unsaturation values with the modulus values as measured by stress-strain testing.

HISTORY

Iodine chloride[3] has been the principal reagent used for the determination of the unsaturation of Butyl polymers. Rehner[4] developed a satisfactory but time-consuming method based on the limiting viscosity of the polymer solution after degradation by ozone. Gallo, Wiese, and Nelson[5] introduced a procedure involving a reaction between the polymer and iodine in the presence of mercuric acetate and trichloroacetic acid. This method is a rapid reproducible test for determining the relative unsaturation of raw isoprene-isobutylene polymers and, with slight modification, was used in this study.

PROCEDURE

A 5.00-gram sample of the polymer weighed on an analytical balance is cut into small pieces and placed in 500 to 600 cc. of C.P. carbon tetrachloride contained in a quart reaction bottle. The bottle is placed in a mechanical shaker and allowed to remain until the sample is completely dissolved (1 to 2 hours). The polymer-carbon tetrachloride solution is then transferred to a 1000 cc. volumetric flask, and the reaction bottle is thoroughly rinsed with carbon tetrachloride. The rinsings are added to the flask, and the contents are made up to volume with carbon tetrachloride and thoroughly mixed by shaking.

Aliquots (100 cc.) of the polymer-carbon tetrachloride solution from the volumetric flask are pipetted into clean, dry 500-cc. iodine flasks. In order, 5 cc. of trichloroacetic acid solution (20 grams of C.P. trichloroacetic acid made up to 100 cc. with C.P. carbon tetrachloride), 25 cc. or iodine solution (12.5 grams of resublimed iodine dissolved in 1 liter of carbon tetrachloride), and 25 cc. of mercuric acetate solution (30 grams of C.P. mercuric acetate in 1 liter of glacial acetic acid) are pipetted into each flask. The flasks are shaken and allowed to stand for exactly 30 minutes in ordinary light.

After reaction, 75 cc. of 7.5 per cent aqueous potassium iodide solution is added to each flask and the contents are titrated with 0.1 N sodium thiosulfate. The iodine in the aqueous layer is titrated until the solution has but a faint yellow tinge. A small amount of 0.5 per cent starch solution is added and the titration is continued dropwise, with vigorous shaking, of the stoppered flask until the colorless end point is reached.

A blank of carbon tetrachloride is run with the sample.

$$\text{Mole \% unsaturation} = \frac{(B - S)(N)\ 1.87}{\text{wt. of sample}} - (0.575 \times \text{weight-\% stabilizer})$$

where B = titration for blank (cc.)
S = titration for sample (cc.)
N = normality of thiosulfate
1.87 = factor derived from the equivalent weight of the structural unit (isobutylene), 3 atoms of iodine per double bond being consumed for tertiary olefins.

As phenyl-2-naphthylamine and AgeRite Stalite, the common stabilizers used in Butyl rubber, react with iodine, a correction (determined experimentally to be 0.575 × weight-% of stabilizer) must be applied to each result.

DISCUSSION OF PROCEDURE

The carbon tetrachloride-iodine solution is unstable in the presence of light. The solution must be blanketed with nitrogen during storage and thoroughly mixed before using.

Although it has been noted[5] that the reaction with iodine-mercuric acetate is complete in about 0.5 hour, the reaction can, under routine test conditions, continue for 8 to 10 hours. However, by carefully controlling the reaction time at 30 minutes, reproducible results can be obtained. This empirical method yields relative unsaturation values suitable for routine control purposes. For reasearch work where absolute unsaturation values are required, the iodine monochloride method developed by Lee, Kolthoff, and Johnson[6] appears to be ideally suited.

Sunlight must be avoided in this test, since extremely high results are obtained when the prepared reaction fiasks are inadvertently placed in direct sunlight. No appreciable difference was noted when samples were tested in total darkness and in ordinary laboratory light.

It has been found advisable to test a standard polymer along with regular samples, so that any discrepancies arising from techniques, solutions, or reaction conditions may be observed.

DEVELOPMENT OF CORRELATION

Since Butyl rubber is usually compounded and vulcanized and the physical properties of the vulcanizates determine the utility of the finished products, the unsaturation values obtained by the method outlined above were correlated with modulus values of the vulcanizates compounded in the carbon black test recipe shown in Table II.

TABLE II

CARBON BLACK TEST RECIPE

	Parts by weight
Butyl polymer	200
MBS standard	
Channel black	100
Zinc oxide	10
Stearic acid	6
Sulfur	4
Mercaptobenzothiazole	1
Tetramethylthiuram disulfide	2
Vulcanization, 40 minutes at 307° F	

Production composites from the commercial unit were tested by both methods during the course of this study, which extended from mid-1950 until the end of 1951. A wealth of data covering all the commercial Butyl grades listed in Table I was accumulated in this manner. The stress-strain testing was carried out according to the specifications for government synthetic rubbers issued by the Reconstruction Finance Corporation[1].

Figure 1 shows the unsaturation values for the low-Mooney grades, corrected for the stabilizer content, plotted against the modulus values. This graph includes the B-1.0, B-2.0, B-3.0, and B-4.0 polymers with a Mooney viscosity of 40–50 (ML 8 minutes at 212° F) and indicates that a straight-line relationship exists between unsaturation and modulus for each grade and for

all grades having the same average Mooney viscosity. Figure 2 shows the correlation derived by plotting the same values for the high-Mooney grade.

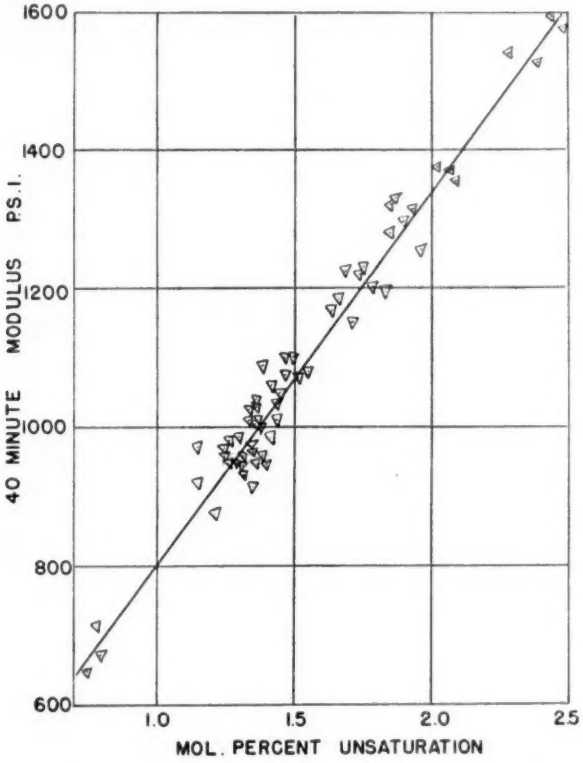

FIG. 1.—Relationship between modulus and unsaturation for low-Mooney Butyl rubber.

Equations to fit the experimental data represented by Figures 1 and 2 have been calculated by the method of least squares and are as follows:

High-Mooney grade (B-2.5)
40-Minute modulus (lb./sq. in.) =

$$478.68 \times \text{mole \% unsaturation} + 484.82 \quad (1)$$

Low-Mooney grades (B-1.0, B-2.0, B-3.0, and B-4.0)
40-Minute modulus (lb./sq. in.) =

$$536.65 \times \text{mole \% unsaturation} + 268.87 \quad (2)$$

Figure 3 combines the experimental correlations established in Figures 1 and 2, and shows that the higher-Mooney polymers possess a lower degree of unsaturation for the same modulus.

EFFECT OF METALLIC STEARATES

The effect of nonpolymeric substances on the correlation has been investigated in this study. All the samples used in this program contained 1.0 to 1.5 weight-per cent stearate, and the correlation established in Figures 1 and 2 is valid only within this range. The effect of stearate has been studied by adding

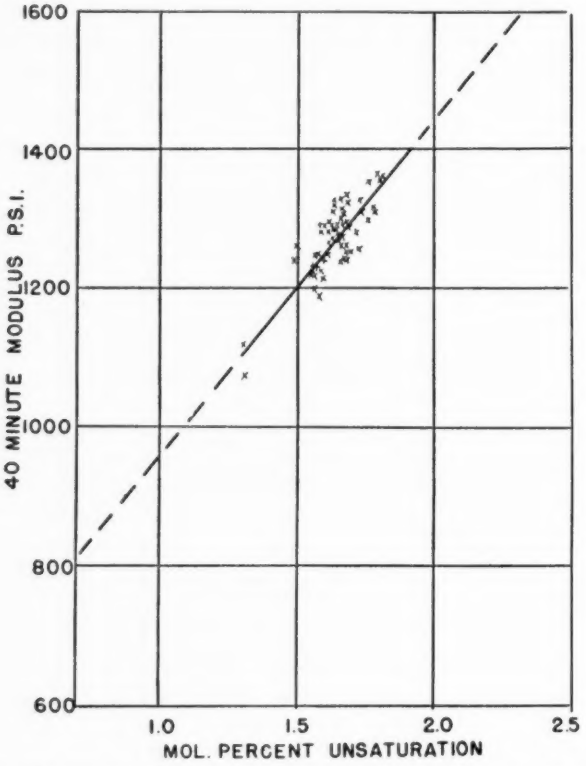

FIG. 2.—Relationship between modulus and unsaturation for high-Mooney Butyl rubber.

zinc stearate in the compounding recipe (Table II) of a low stearate polymer. Table III shows that the determined modulus, using the revised recipe, agrees

TABLE III

EFFECT OF STEARATE ON MODULUS VALUES

Sample	I	II
40-Minute modulus (lb./sq. in.)		
Predicted from unsaturation	1235	1015
By stress-strain (0.4% stearate in polymer)	1285	1070
By stress-strain (stearate increased to 1.5%)	1225	1035

with that predicted by unsaturation values based on polymers of high stearate type. It is concluded that the stearate content of the polymers decreases the modulus, measured by stress-strain testing, but has no noticeable effect on the unsaturation values.

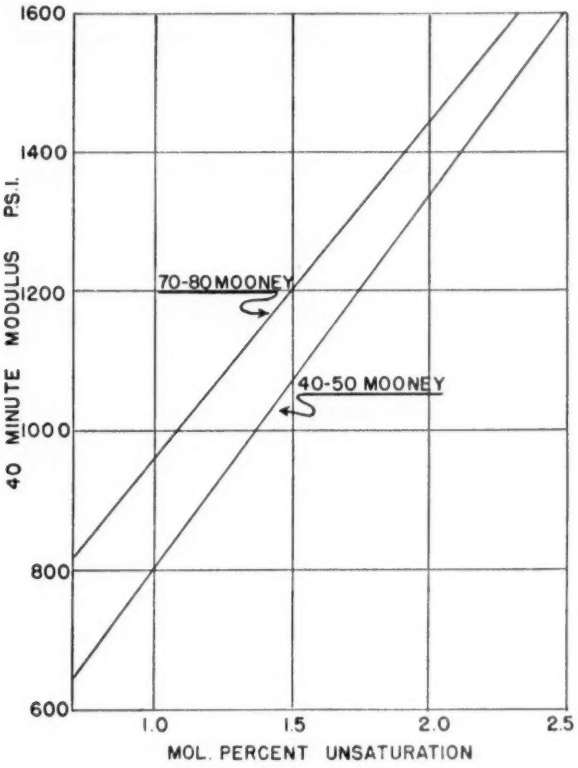

FIG. 3.—Effect of Mooney on modulus-unsaturation relationship of Butyl rubber.

EFFECT OF MOONEY SCORCH

The initial cure time of Butyl rubber, as measured by the Mooney scorch value obtained using the gum test recipe[7] (Table IV), has been suggested for

TABLE IV

GUM TEST RECIPE

	Grams
Polymer	200
NBS standard	
Zinc oxide	4
Tetramethylthiuram disulfide	1.2
Sulfur	4
	209.2

predicting the curing properties of the polymer, and it has been shown[5] that nonpolymeric components *i.e.*, aluminum chloride, sodium stearate, etc., markedly affect the Mooney scorch values, using this recipe. Butyl samples having Mooney scorch times from 8 to 26 minutes have been studied, and there is no indication that the initial curing time in the gum recipe affects the accuracy of this unsaturation-modulus correlation. The normal Mooney scorch range is much narrower than the range covered in this study, and it is concluded that Mooney scorch can be ignored in the application of this correlation.

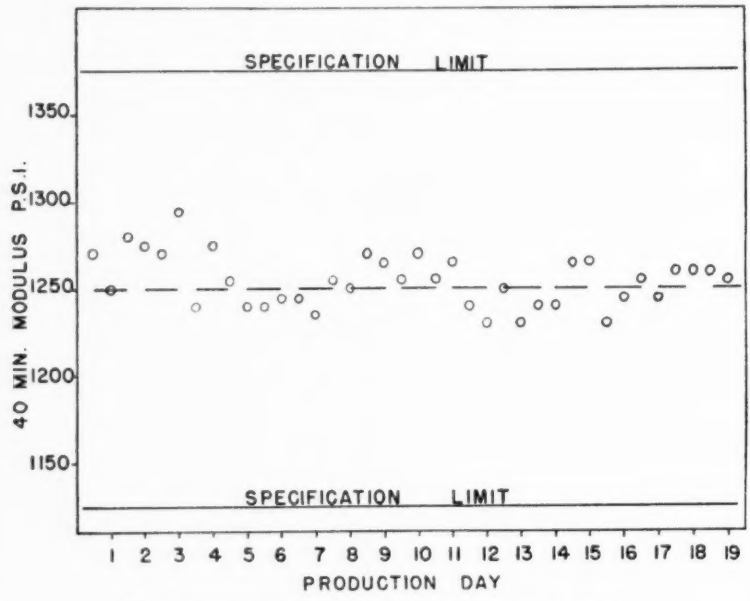

FIG. 4.—Typical quality control chart for Butyl rubber production.

REPRODUCIBILITY OF METHOD

Table V shows the modulus values (predicted by unsaturation) on a single sample of standard Butyl polymer. These values were obtained on a routine basis over a 1-month period, one sample being tested each day by a single operator. The standard deviation calculated for this data is 12 lbs. per sq. in., compared with the standard deviation of 20 lbs. per sq. in. for the stress-strain

TABLE V

40-MINUTE MODULUS (PREDICTED BY UNSATURATION) ON STANDARD BUTYL POLYMER A

1225,	1235,	1225,	1225,	1230,	1225,	1230,	1255,	1230,	1215,	1235,
1225,	1230,	1240,	1215,	1240,	1225,	1255,	1235,	1210,	1200,	1230,
1215,	1225,	1210,	1235,	1225,	1224,	1215,	1220,	1210		

Average value (lb./sq. in.)	1225
No. of tests	31
Standard deviation (lb./sq. in.)	12

values on a standard Butyl polymer shown in Table VI. The F value for the data shown in Tables V and VI is 2.8, while the critical value from the F tables is 2.38. Thus it can be concluded that the standard deviation of the unsaturation is significantly lower than the standard deviation of the stress-strain data.

APPLICATION OF CORRELATIONS

The unsaturation method of predicting the modulus level of Butyl rubber, based on the correlations established in Figures 1 and 2, can be used for plant control. Composite and spot samples may be analyzed by the procedure out-

TABLE VI

40-MINUTE MODULUS (DETERMINED BY STRESS–STRAIN) ON STANDARD BUTYL POLYMER B

1295,	1315,	1315,	1285,	1275,	1295,	1265,	1265,	1265,	1295,	1275,
1315,	1305,	1305,	1315,	1285,	1305,	1315,	1295,	1325,	1305,	1315,
1315,	1325,	1355,	1315,	1285,	1285,	1295,	1315			

Average value (lb./sq. in.)	1300
No. of tests	30
Standard deviation (lb./sq. in.)	20

lined and reliable results reported in 3 to 4 hours after the samples are prepared. The availability of this information has made the commercial production of Butyl rubber ideally suited for quality control. Using normal control charts with inner control limits established within the specification band, a marked improvement in product uniformity has been achieved. Figure 4, a reproduction of one of these charts, illustrates the excellent control which can be attained using modulus by unsaturation values. At the same time stress-strain testing, for plant control purposes, can be drastically reduced.

TABLE VII

DATA OBTAINED BY UNSATURATION AND STRESS–STRAIN

	40-Minutes modulus (lb./sq. in.)		
Sample	By unsaturation	By stress-strain	Difference
1	1325	1300	+25
2	1315	1350	−35
3	1280	1280	--
4	1250	1240	+10
5	1250	1255	− 5
6	1250	1275	−25
7	1265	1260	+ 5
8	1285	1245	+40
9	1270	1260	+10
10	1265	1290	−25
11	1240	1265	−25
12	1260	1255	+ 5
13	1245	1220	+25
14	1295	1320	−25
	Average difference		19
	Standard deviation of differences		23

Table VII shows a comparison of modulus values obtained by both unsaturation and stress-strain of fourteen consecutive production composites. On a routine basis, the values by unsaturation and by stress-strain testing agree within the experimental error of the latter test. As the average difference

and the standard deviation of the differences are very close to the same value, it can be concluded that the same value is being obtained by each method.

SUMMARY

The stress-strain method of determining the modulus of Butyl rubber possesses severe shortcomings when applied to plant control, the most serious being the time lag in reporting reliable results. A chemical method is described which is less time-consuming and at the same time is more reproducible. The basic iodine-mercuric acetate method for Butyl unsaturation has been improved by the standardization of reaction conditions, and a correlation between unsaturation and stress strain values in the National Bureau of Standards formula has been developed. This comprehensive study has covered commercial grades of Butyl rubber over an 18-month period. The application of the method to plant control is described, and improved product uniformity is indicated. Reliable results suitable for control purposes are available in 3 to 4 hours.

ACKNOWLEDGMENT

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QUANTITATIVE DETERMINATION OF COPPER IN NATURAL RUBBER *

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This paper describes the method currently in use at the National Bureau of Standards for the determination of copper in natural rubber and latex. It involves the dry-ashing procedure for the destruction of organic matter and subsequent preparation of a copper carbamate complex, which is measured colorimetrically by means of Nessler tubes or by a photoelectric photometer. The procedure was formulated as a result of considerable experimentation with existing methods of copper analysis and with techniques used in other rubber procedures. It incorporates those portions of existing methods which have been found to be the most suitable with respect to accuracy and simplicity. The present investigation includes the study of some possible sources of error in the method of analysis. It also compares the wet digestion with the dry ashing methods of destruction of organic material.

A number of different procedures have been published for the determination of copper in rubber. Because of its greater simplicity, the dry-ashing technique is often used in many laboratories in spite of the fear of losing some of the copper. Several authors[1] recommend burning the rubber at as low a temperature as possible. Many others, however, believe that copper may quite easily be lost during any ignition procedure, and, as a result, standardization organizations usually recommend the wet-oxidation method[2].

Most analytical determinations for small amounts of copper involve a color reaction. Several complex-forming reagents for the color reaction have been studied[3], but sodium diethyldithiocarbamate, probably first used by Callan and Henderson[4], is the reagent most frequently used. Zinc diethyldithiocarbamate has been recommended by Poulton and Tunnicliffe[5] because of its greater solubility in organic solvents than the sodium salt, but it is not generally available. While the colorless zinc carbamate complex can be used as a reagent in place of the sodium carbamate salt, zinc salts in quantities normally found in compounded rubber interfere with the formation of the copper complex. This interference by zinc is not easily detected, and cannot be avoided except by separating the metals.

Van der Bie[6] separates copper from the interfering elements by microelectrolysis or by precipitation as the sulfide. Several authors[7] recommend the removal of manganese by precipitation as the dioxide in ammoniacal solution, though judging by Dekker's results[8], the amount of manganese usually found in rubber (less than 0.001 per cent) would not interfere with the copper analysis. Cassagne[9] uses disodium phosphate in an ammoniacal medium to form a complex with iron, and then extracts the copper complex from the aqueous solution by means of ether or isoamyl alcohol. The method most often used for

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separation of the iron involves its precipitation as the hydroxide, but this procedure has the disadvantage of tending to remove some of the copper with the precipitate[8].

Since cyanide solutions decolorize copper carbamate solutions without affecting the color of iron or manganese carbamate, the color due to copper can be taken as the difference between that of the carbamate solution and that of the solution subsequently treated with cyanide[5]. This procedure is more rapid than physically separating the iron and the copper, and would be a recommended procedure if large quantities of manganese or iron are present in the rubber.

Fowler[10] presents a procedure for latex rubber which closely resembles the one recommended here, but he does not report its limitations and possible inaccuracies.

RECOMMENDED PROCEDURE

The procedure recommended for the determination of copper in the rubber is as follows.

A 10-gram sample of rubber is weighed, wrapped in a 15-cm. piece of ashless filter paper, and placed in a No. 2 Coors porcelain crucible (50 cc.) with clean unetched inside walls. The crucible is placed in a muffle furnace maintained at 550° C, and the door is closed. Since inflammable vapors are evolved, the furnace should not be opened during the first hour.

The sample is ashed until no carbon specks are visible. This usually requires from two to three hours. The crucible is removed and cooled, and 30 cc. of a mixture of one part concentrated nitric acid to two parts of water is added. The contents of the crucible are digested on the steam bath for one-half to one hour, transferred to a beaker, diluted to 150 to 250 cc., and filtered. Twenty cc. of 15% citric acid is added to the filtrate, and the solution brought to pH 9 by adding a mixture of equal quantities of water and concentrated ammonia.

The solution is cooled, and 20 cc. of an aqueous solution of 0.1% sodium diethyldithiocarbamate is added. The suspension is allowed to stand 10 to 20 minutes, and is then extracted with three or four 10-cc. portions of carbon tetrachloride. The last extract should be colorless. The extracts are combined in a glass stoppered bottle, and dried by shaking with a few grams of anhydrous sodium sulfate.

After standing for one-half to one hour, the solution is filtered into a 100-cc. volumetric flask along with a two or three 10-cc. rinsing of the desiccant. The solution is then made up to volume with carbon tetrachloride, and the absorption determined by the use of a Fisher electrophotometer and its standard blue filter, which has a maximum transmission at 425 millimicrons.

The maximum absorption of the carbamate complex occurs at approximately 440 mμ, but a filter of broad transmission is satisfactory and green filters are recommended rather than blue when visual photometers are used, because of the increased visual acuity at the longer wave-length[11].

A blank consisting of the reagents is carried through the procedure with each group of samples.

The carbamate reagent solution should be protected from light and renewed every two or three weeks. A pronounced thiol odor indicates that the carbamate has decomposed, and fresh reagent should be prepared. The solutions containing the copper complex should be protected from light, and an

occasional sample checked after two hours to determine if fading is occurring. When fading does occur, it can usually be blamed on old and presumably weakened solutions of carbamate.

A calibration curve of the electrophotometer, using the A-scale reading for absorbancy vs. copper content, is established by using the reagents to be used in the analyses and adding to the nitric acid solution 0, 1, 2, 5, and 10-cc. portions of freshly prepared copper sulfate solution containing 0.00001 gram of copper per cc. This dilute solution is stable for several months if 0.1 to 1.0% sulfuric acid is added and the solution is kept in pyrex glass[12]. With carbon tetrachloride, the maximum A-scale reading, using the standard 23-cc. cells with a 22-mm. path, should be less than 30 if the absorption curve is to be a straight line. Aliquots should be taken of samples which contain more than 0.00005 gram of copper.

Although most of the analyses for copper in rubber latexes done in the course of this work have been performed by ashing dried films of rubber made from these latexes, a more recent and simpler procedure is recommended which ashes the liquid latex directly. A weighed sample of latex is placed in a cone of ashless filter paper in a porcelain crucible, and sufficient ashless filter pulp is added to absorb the latex. The ashing procedure is then followed as previously described. Detailed procedures for the recommended ashing methods of both dry rubber and rubber latex are described in another publication[13].

EXPERIMENTAL WORK

Various experiments and analyses were performed in order to study possible sources of error in the procedures.

Loss of copper on ashing.—By heating 1-gram samples of copper chloride salt at 550° C, it was found that the loss of weight amounted to about 1 per cent per hour. The double chloride of copper and potassium, $CuCl_2 \cdot 2KCl$, at 550° C evaporated or decomposed at a rate of 0.3 per cent per hour. When using milligram portions of the double chloride, and determining the copper content colorimetrically, the loss of copper during 18 hours of heating at this temperature amounted to only 5 per cent total, or about 0.3 per cent per hour.

It was found that the ash from the rubber samples had a tendency to stick tightly to the walls of etched crucibles, and that the copper could not always be dissolved quantitatively. A similar difficulty with etched silica crucibles was reported by Conerie[14]. A few tests, using platinum crucibles, also indicate incomplete recovery of copper from the ash. It is, therefore, recommended that porcelain or Vycor crucibles be used and that they be replaced by new ones when the inside surface has become etched. A pad of ashless filter pulp or paper under the sample prolongs the useful life of the crucible.

A comparison was made between the dry-ashing and the wet-oxidation procedures, using 10-gram samples of pale crepe rubber with known quantities of added copper. Both methods made use of measuring the absorption of carbon tetrachloride solutions of the copper carbamate complex. Results of the analyses for copper, expressed in parts per million, are as follows:

Sample	A	B	C	D
Cu added	0	10	50	100
Cu found by dry-ashing	3.0	13.0	54.2	104.5
Cu found by wet-oxidation	3.0	13.0	55.0	104.5

Other samples of rubber with no added copper were analyzed for copper by the same two methods, with the following results.

Sample	E	F	G	H
Cu found by dry-ashing	3.0	3.3	5.1	6.1
Cu found by wet-oxidation	3.3	3.3	5.4	6.0

Comparisons of the results in the above data show that there is no significant difference between the results obtained by the dry-ashing procedure and those obtained by wet oxidation, and that if copper is lost during the dry ashing procedure, it is not measurable.

When the organic matter of the rubber was to be destroyed by wet oxidation, a procedure of the British Standards Institution was used[15]. The sample was heated with nitric acid in a Kjedhal flask. After the first reaction had subsided, sulfuric acid was added to the solution, and portions of nitric acid were added when the refluxing solution darkened. When the solution ceased to change color on loss of nitric acid, portions of hydrogen peroxide solution were added to the slightly cooled acid solution until the color of organic material was destroyed.

Error from iron contamination.—The A.S.T.M. procedure[16] requires the removal of iron by precipitation before preparing the copper carbamate. The solution from the acid digestion is neutralized with ammonia. The iron precipitated as removed by filtration, redissolved, and reprecipitated to remove adsorbed copper. This loss may not always be recovered completely by performing the extra steps of redissolving and reprecipitating the iron, as is shown below:

Sample	Treatment of iron	A-Scale reading carbamate complex extracted with CCl_4	Recovery of copper (%)
Reagent (blank)	—	4.1, 4.3	—
0.014 gram Fe	Citrate added	4.3, 4.3	—
0.0001 gram Cu	—	17.3, 17.3	—
Cu and Fe	Citrate added	17.5, 17.1	100
Cu and Fe	Precipitated	12.0, 14.0	65, 75

The presence of iron in the rubber also gives a color which influences the reading of the absorbancy of the copper-carbamate complex, even in the presence of citric acid. It was found by experiment that in an aqueous dispersion with added citrate, iron has about 1 per cent as much effective absorption as copper. This is illustrated by the following data, in which measured quantities of the copper and iron are compared visually as aqueous dispersions to give equivalent color:

Concentration of solution	Visual equivalents of solutions			
	A	B	C	D
Cu, 0.00001 g. per cc.	0.2 cc.	0.4 cc.	0.6 cc.	1.0 cc.
Fe, 0.001 g. per cc.	0.3	0.5	0.7	0.9

However, when the complex has been extracted by carbon tetrachloride, a much higher ratio (of the order of a thousand) of iron to copper in the original sample of rubber is required to produce an equivalent color. This was shown by an experiment in which the same iron and copper solutions were used as before, the concentration of the iron solution being 100 times that of the copper

solution. The absorbancy of different quantities of these solutions made up to the same volume are given in the following table:

	A	B	C	D	E
Volume of metal solution (cc.)	0	2.0	4.0	6.0	8
A-Scale reading Cu solution (corrected for blank)	0	7.5	18.3	27.5	38
A-Scale reading Fe solution (corrected for blank)	0	1.0	2.0	3.0	Fog
Ratio	–	7.5	9.1	9.1	—

This agrees approximately with the results of Poulton and Tunnicliffe[5].

Error caused by variation in the color of aqueous dispersions.—The A.S.T.M. procedure measures the color of the carbamate complex in the aqueous medium, which is prevented from settling by the addition of a protective colloid such as gum arabic. However, absorption measurements on dispersions in aqueous media are difficult to reproduce from one time to another, varying with very slight differences in the reagents or the manner of preparation. Procedures in which the absorption of a solution of the complex was determined in an organic solvent were found to be more reproducible.

In the procedure recommended here, the carbamate complex was extracted from the aqueous solution by carbon tetrachloride. Other solvents, such as butyl acetate and petroleum ether, were also found to be satisfactory. The complex is more soluble in butyl acetate than in carbon tetrachloride, and is less soluble in petroleum ether. Petroleum ether does not extract the complex from water dispersion except in the presence of a large excess of citric acid. The carbon tetrachloride extraction is not only easily performed, but its extract is more easily dried than those made with the other solvents.

Error caused by fading of color of carbamate complex solution.—It was found necessary to have the carbon tetrachloride solution dry before absorbancy measurements are made. During the drying process the absorbancy decreases as much as three A-scale units as the turbidity of the solvent is decreased by the removal of water. After the solvent has been dried, the absorbancy does not change appreciably for several hours, if the recommended procedure is used. In 24 hours the fading produces a decrease of absorbancy of from 10 to 20 per cent. The addition of a large excess of carbamate is recommended in the procedure in order to avoid fading in the course of the determination.

CONCLUSIONS

A procedure is recommended in which small amounts of copper in rubber can be measured quantitatively by determining the depth of color of a copper carbamate complex in a carbon tetrachloride solution. The complex is formed in an alkaline solution prepared from an acid extract of the rubber ashed at 550° C. This procedure yields results which are as reliable as those obtained by the more tedious and time-consuming procedures involving the wet-oxidation process which are at present recommended by standardizing organizations.

The use of an organic solution rather than an aqueous suspension gives better reproducibility, permits easier use of a photometer, and reduces the interference due to iron by a factor of ten.

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SMALL AMOUNTS OF COPPER IN DYES AND RUBBER CHEMICALS

COLORIMETRIC DETERMINATION WITH ZINC DIBENZYLDITHIOCARBAMATE *

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The method in use in this laboratory for the determination of small amounts of copper (together with a method for manganese in the same sample) in dyes and other organic materials was described in 1940 by Palfrey, Hobert, Benning, and Dobratz[1]. Sulfuric and nitric acids and hydrogen peroxide are employed for destruction of organic matter, and copper is determined by measurement of the intensity of color developed with sodium diethyldithiocarbamate in an ammoniacal medium. Although provision is made for preliminary separation from a number (but not all) of the interfering metals, the separations involving filtrations are troublesome, and there has often been a question whether copper is completely recovered. Even small quantities of nickel, cobalt, and bismuth interfere, provided they exceed somewhat the amount of copper. A better method was needed.

The advantages of extraction of copper diethyldithiocarbamate into an immiscible organic solvent have been summarized by Sandell[2]. It seemed likely that many interferences might be eliminated if extraction could be made from acid rather than from ammoniacal solution, as is usually done. Because sodium diethyldithiocarbamate appeared to be too unstable to be used with acid solution, a search was made for other dithiocarbamates which might be sufficiently stable, sensitive, and selective.

Selection.—A number of dithiocarbamates were tried as reagents in water, chloroform, or carbon tetrachloride solutions of varying concentrations. The most generally satisfactory reagent investigated is a 0.01 per cent solution of zinc dibenzyldithiocarbamate in carbon tetrachloride. The reasons for this choice are the stability both of the reagent and the extracted yellow copper salt, a sensitivity for copper which is at least equal to that of other reagents tested, speed and completeness of extraction with a small excess of reagent, few interferences, and the use of carbon tetrachloride as a solvent which has negligible solubility in water.

Stability.—After standing for 2 months in a clear borosilicate glass bottle in diffuse light, the 0.01 per cent solution remained clear and the reagent blank was unchanged, although the reagent had lost about 10 per cent of its ability to extract the maximum amount of copper. No other reagent tested was found to be as stable. The 0.01 per cent solution has never given evidence of instability in contact with 1 *N* sulfuric acid, from which extraction is normally made.

No change in the intensity of color of copper dibenzyldithiocarbamate solu-

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tions in carbon tetrachloride was ever observed on exposure to the light of the photometer, or to direct sunlight for 1 hour.

Although the desired copper limit of the range is about 40 micrograms, all copper present, up to at least 60 micrograms, is usually extracted after 30 seconds of vigorous shaking.

Preparation.—Zinc dibenzyldithiocarbamate may be purchased under the name of Arazate from the Naugatuck Chemical Co., Naugatuck, Conn., and is suitable for use as a reagent. Lower blanks and more rapid extractions have been obtained, however, with reagent prepared in the laboratory from purified sodium dibenzyldithiocarbamate. The latter was prepared by the reaction of dibenzylamine, carbon disulfide, and sodium hydroxide. The water in soluble zinc salt was precipitated by adding copper-free zinc sulfate solution to an aqueous solution of the sodium salt. The zinc salt (dried in a vacuum oven at 40° C) analyzed 58.26% carbon, 4.54% hydrogen, 4.42% nitrogen, 21.11% sulfur, 10.47% zinc; theory, 59.05% carbon, 4.63% hydrogen, 4.59% nitrogen, 21.02% sulfur, 10.72% zinc.

INTERFERENCES

Metallic ions.—Metallic ions investigated included the common known interferences in procedures using sodium diethyldithiocarbamate, as summarized by Sandell[2], as well as others listed by Callan and Henderson[3] which in large amount give turbidity or color with sodium diethyldithiocarbamate.

Ten cc. of 0.01 per cent zinc dibenzyldithiocarbamate in carbon tetrachloride was shaken for 30 seconds with approximately 1 *N* sulfuric acid solutions of metallic salts containing 0.5 gram of various metals. No reading as copper and no visible color were obtained from the following ions: aluminum, antimony (III), antimony (V) (0.1 gram), arsenic (III), arsenic (V), cadmium, calcium, chromium (III), iron (II), lead, magnanese (II), mercury (II) (0.2 gram), silver (0.001 gram), tin (IV), uranyl, and zinc.

The interfering metals and the magnitude of the interference are given in Table I.

TABLE I

EXTENT OF INTERFERENCE FROM METALS THAT MIGHT BE REPORTED AS COPPER

Interfering ion	Amount (g.)	Recovered as copper (γ)	Color of extract
Bi^{+++}	0.001	11.2[a]	Yellow
Bi^{+++}	0.0001	5.6	
Ni^{++}	0.5	5.4	Green-yellow
Ni^{++}	0.05	1.1	
Ni^{++}	0.01	0.2	
Co^{++}	0.5	4.4	Green-yellow
Co^{++}	0.01	0.3	
Fe^{+++}	0.5	0.6[b]	
Fe^{+++}	0.05	0.0	

[a] No higher value obtained from as much as 0.1 gram of bismuth.
[b] 1.2γ recovered as copper on shaking 3 minutes.

The possibility of interferences from the same metallic ions to prevent the recovery of copper was investigated by extraction from 1 *N* sulfuric acid solution containing known small amounts of copper in addition to larger amounts of the various other metallic ions. These results are summarized in Table II.

Separation from nickel and cobalt.—Nickel and cobalt are easily recognized by the strong color they contribute to the aqueous solutions when they are present in large enough amounts to interfere. Separations, when necessary, can be made as follows:

Make an extraction as usual and transfer all of the carbon tetrachloride layer to another separatory funnel, rinsing the contents of the first funnel with

TABLE II

RECOVERY OF COPPER IN PRESENCE OF OTHER METALLIC IONS

Foreign ion	Amount (g.)	Copper present (γ)	Copper recovered (γ)
Al^{+++}	0.5	5.0	5.0
Sb^{+++}	0.1	5.0	0.7
Sb^{+++}	0.01	5.0	4.5
Sb^{+++}	0.01	40.0	31.7
Sb^{+++++}	0.1	5.0	1.4[a]
Sb^{+++++}	0.01	5.0	4.0[a]
As^{+++}	0.5	5.0	5.0
As^{+++++}	0.5	5.0	5.0
Bi^{+++}	0.01	5.0	12.4[b]
Bi^{+++}	0.01	40.0	16.3[b]
Bi^{+++}	0.0001	5.0	11.6[c]
Bi^{+++}	0.0001	40.0	46.0[c]
Cd^{++}	0.5	5.0	4.9
Ca^{++}	0.5	5.0	4.6[d]
Cr^{+++}	0.5	5.0	5.0
Co^{++}	0.05	5.0	4.7
Co^{++}	0.05	40.0	37.8
Fe^{++}	0.5	5.0	5.0
Fe^{+++}	0.5	5.0	5.5
Pb^{++}	0.5	5.0	5.1[e]
Mn^{++}	0.5	5.0	5.0
Hg^{++}	0.001	40.0	0.0
Hg^{++}	0.0001	5.0	5.2
Hg^{++}	0.0001	40.0	36.2
Ni^{++}	0.05	5.0	5.9
Ni^{++}	0.05	40.0	41.5
Ag^{+}	0.001	5.0	0.0
Ag^{+}	0.0001	5.0	5.0
Ag^{+}	0.0001	40.0	40.0
Sn^{++++}	0.5	5.0	5.0
UO_2^{++}	0.5	5.0	4.9
Zn^{++}	0.5	5.0	5.0

[a] Antimony introduced as trivalent and carried through digestion procedure before extraction.
[b] Principally bismuth appearing as copper (see Table I), with preferential reaction and extraction with bismuth.
[c] Evidently sufficient reagent present to react with all or nearly all bismuth and copper.
[d] Digestion made with calcium and copper; extraction made in presence of precipitated calcium sulfate, with no difficulty in separating enough carbon tetrachloride layer for measurement.
[e] No digestion made, extraction easily made in presence of precipitated lead sulfate.

carbon tetrachloride and adding it to the extract. All the copper together with a small amount of the interference is now in the carbon tetrachloride. Add 30 cc. of copper-free water, 5 cc. of 8 *N* sulfuric acid, and 2 cc. of 0.5 *N* potassium permanganate, shake for a few seconds, and let clear. Permanganate easily destroys the dibenzyldithiocarbamate complexes and excess reagent, leaving colorless decomposition products. Add 3 cc. of 10 per cent hydroxylamine hydrochloride solution, shake briefly, and let stand for 5 minutes, making sure that no trace of permanganate (or manganese dioxide around the stopper or

stopcock) is left. Discard the carbon tetrachloride layer, extract with a fresh portion of reagent, and read for copper.

Recovery of copper by this procedure is shown in Table III.

TABLE III

COPPER RECOVERY AFTER SEPARATION FROM 0.5 GRAM OF NICKEL OR COBALT

Interfering ion	Amount (g.)	Copper added (γ)	Copper recovered (γ)
Ni^{++}	0.5	0.0	0.6
Ni^{++}	0.5	5.0	5.4
Co^{++}	0.5	0.0	0.6
Co^{++}	0.5	5.0	4.3

Separation from bismuth.—An inspection of Tables I and II shows that the tests for interference in the general procedure may fail for amounts of bismuth that will be all removed in the first extraction along with copper, and a maximum error of 11 micrograms as copper might result when no copper is present. The following procedure may be employed where bismuth interference must be eliminated. It depends on the fact that bismuth is not easily extracted from strong hydrochloric acid solution, while complete extraction of copper is possible with somewhat longer than usual shaking.

To the sulfuric acid solution containing bismuth and copper, add 5 cc. of concentrated hydrochloric acid for each 30 to 40 cc. of solution. Make an extraction as usual and transfer all the carbon tetrachloride layer to another separatory funnel, rinsing the contents of the first funnel with carbon tetrachloride and adding it to the extract. All of the copper, together with a small amount of bismuth, is now in the carbon tetrachloride. Add 5 cc. of 8 *N* sulfuric acid and 2 cc. of 0.5 *N* potassium permanganate, shake for a few seconds, and let clear. Add 3 cc. of 10% hydroxylamine hydrochloride solution, shake briefly, and let stand for 5 minutes. Add 25 cc. of concentrated hydrochloric acid and then discard the carbon tetrachloride. Extract with a fresh portion of reagent, shaking for 3 minutes instead of the usual 30 seconds, and read for copper.

Recovery of copper by this procedure is shown in Table IV.

TABLE IV

COPPER RECOVERY AFTER SEPARATION FROM BISMUTH

Amount of bismuth (g.)	Amount of copper (γ)	Recovery of copper (γ)
0.1	0.0	0.3
0.1	5.0	5.4
0.1	40.0	39.0

Elimination of interference from mercury, silver, and antimony.—Mercury, silver, and antimony above limiting concentrations (Table II) prevent complete extraction of copper, apparently by formation of colorless dibenzyldithiocarbamates, which are extracted preferentially or along with the copper salt. These interferences may be eliminated by use of enough reagent, *i.e.*, a more concentrated solution, to combine with all of the copper in addition to the interfering ions. The main objection is that more reagent increases the amounts of the colored nickel, cobalt, bismuth, and iron dibenzyldithiocarbamates which extract when these metals are present.

Interference from mercury may be reduced by addition of potassium bro-

mide, as in the procedure of Laug and Nelson[4] for separation of mercury from copper dithizonate. There is no interference from 0.01 gram of mercury in the recovery of 40 micrograms of copper if 5 cc. of 40 per cent potassium bromide is added before extraction, although 3 minutes of vigorous shaking are required.

GENERAL METHOD

Weigh the sample into an 800-cc. Vycor Kjeldahl flask. Take approximately 1 gram of sample if copper alone is to be determined (or approximately 5 grams if manganese is to be determined as well). Add 10 cc. of concentrated sulfuric acid and one or two glass beads, and heat carefully on the digestion rack until charring begins. Add 5 cc. of concentrated nitric acid and continue the digestion, adding further small amounts of nitric acid as charring recurs. Add more sulfuric acid, if necessary, in order to keep the entire sample wet. When successive additions of nitric acid fail to produce further lightening of color in the digest as it is boiled down to sulfur trioxide fumes, cool somewhat, carefully add 5 cc. of hydrogen peroxide, and boil again to sulfur trioxide fumes. Continue adding small portions of hydrogen peroxide until there is no further change in appearance of the digest. Cool somewhat, add 50 to 100 cc. of copper-free water, boil down again to sulfur trioxide fumes, and continue until not more than 5 ml. of sulfuric acid remains. Cool, dilute to about 50 cc. with copper-free water, and cool again.

Without filtering, transfer the whole digest, or an aliquot that preferably contains no more than 40 micrograms of copper, to a 250-cc. separatory funnel and dilute to about 100 cc. with copper-free water. Add 10 cc. of zinc dibenzyldithiocarbamate reagent by pipet or buret and shake vigorously for 30 seconds (longer if experence has shown the necessity for it with the reagent used). Withdraw the carbon tetrachloride layer through absorbent cotton into a 1-cm. photometer cell, reserving the acid solution for a manganese determination if desired. Measure the per cent transmittance at 435 mμ, using carbon tetrachloride as a reference liquid. Carry a blank determination through the entire digestion and extraction procedure. Determine the amount of copper in the sample and blank by reference to a standard curve which should be prepared to cover the range from 0 to 60 micrograms of copper.

In applying the method to unknown samples or to materials of a type not previously analyzed, and which may contain elements whose interference effects have not been determined, one extraction should be made following the apparent removal of copper, since a test for interference which may give high results. If little or no copper was extracted, a test for inhibiting interferences also should be made by adding a known amount of copper and making a further extraction to determine its recovery.

DISCUSSION

The wet oxidation of the earlier method[1] has been simplified as the result of several years of experience. The principal difference consists in the use of concentrated instead of fuming nitric acid, which often contains objectionably high amounts of impurities.

Contamination during digestion has been the greatest source of error. It is of the utmost importance that the mouths of the flasks do not touch the digestion rack, and that all fumes be drawn directly into a hood which provides no opportunity for reflux outside the flask.

Ten cc. of the 0.01 per cent solution was chosen as the standard amount to

be used, because it provides sufficient reagent to show an amount of copper in excess of the normal range and to react with and prevent the interference of small amounts of mercury, silver, or antimony. At the same time, the excess is not great enough to mistake for copper any known metal that has not already revealed its presence by its color in solution, with the exception of bismuth, which would interfere in any case, as it reacts preferentially.

Although a number of different kinds of materials have been successfully analyzed, the main application of the method has continued to be in the analysis of rubber chemicals, where determination of manganese as well as copper is invariably required. Manganese is determined in the acid solution following extraction, using periodate oxidation in a procedure similar to the earlier method[1], except that a photoelectric colorimeter is used for measurement of per cent transmittance at 525 mμ.

Results are usually accurate and reproducible within 0.5 microgram, based on over-all recovery of copper taken through the wet oxidation and extraction procedure. Because in the absence of interferences, as shown in Table II, the recovery of copper through the extraction procedure alone is usually complete within 0.1 microgram, it is assumed that the limiting factors are contamination or losses accompanying wet oxidation. Blanks on reagents usually show between 0.5 and 1.5 micrograms of copper, the major portion of which is derived from the nitric acid.

The method has been in use in essentially its present form for eighteen months.

SUMMARY

This work was undertaken to provide a more specific method for the routine determination of small amounts of copper in rubber chemicals, dyes, and dyed fabrics. A dithiocarbamate type of reagent—a 0.01 per cent solution of zinc dibenzyldithiocarbamate in carbon tetrachloride—will selectively extract copper from acid solutions containing relatively large amounts of most other metals. The method is accurate and reproducible to about 0.5 microgram in the range of 0.5 to 40 micrograms of copper. No precipitations or filtrations are required. The reagent is commercially available, the reagent solution and the color of the extracted copper dibenzyldithiocarbamate are stable, and the acid solution remaining after extraction may be used to determine other metals. Because copper dibenzyldithiocarbamate is selectively extracted from solutions containing relatively large amounts of many other metallic ions, the reagent may be used to determine small amounts of copper in metals and their salts.

ACKNOWLEDGMENT

The authors are indebted to S. W. Rumbel of the Pigments Department of the company for calling their attention to the availability of zinc dibenzyldithiocarbamate and suggesting that a trial be made to see if it possessed any advantages over the sodium salt then in use. The development of the method and extensive testing have been made possible by the cooperation of many members of the analytical staff of this laboratory.

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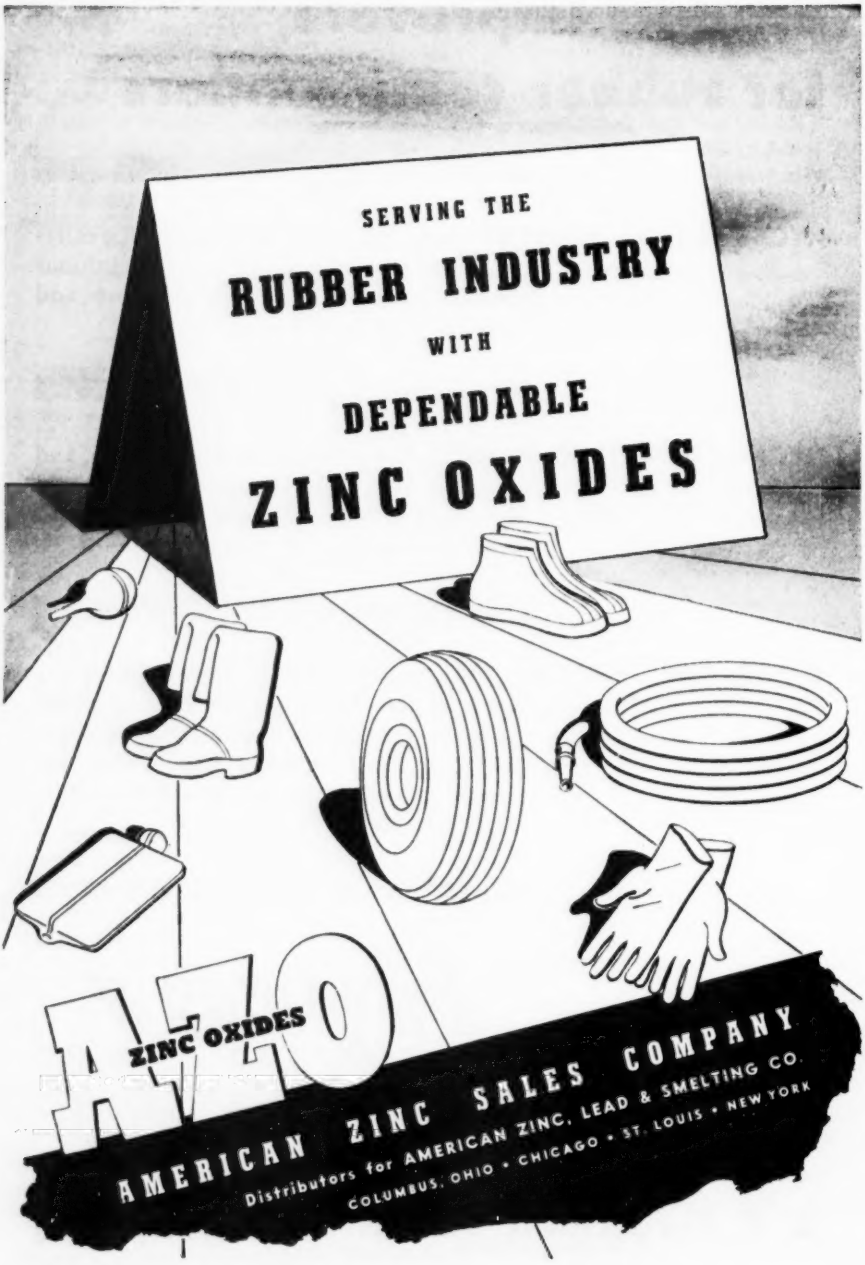
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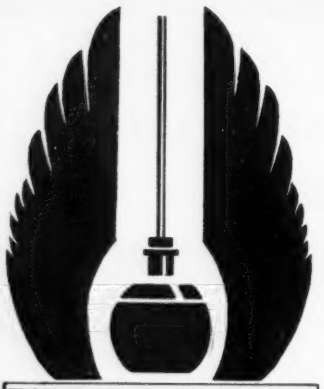

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... Because the Horse Head line comprises the most complete family of Zinc Oxides for rubber:

1. It is the only line having such a wide range of particle sizes, surface conditions and chemical compositions.
2. Its *conventional* types cover the range of American and French Process oxides.
3. Its *exclusive* types include the well-known Kadox and Protox brands.

That means you need not waste time adapting a single Zinc Oxide to each specific compound. Instead, just choose from the Horse Head line the Zinc Oxides that best meet your needs.

FORMULATE *BETTER!*

... Because you need to compromise less when you choose from the wide variety of Horse Head Zinc Oxides.

... Because the Horse Head brands can improve the properties of your compounds.

Year after year, for nearly a century, more rubber manufacturers have used more tons of Horse Head Zinc Oxides than of any other brands.

THE NEW JERSEY ZINC COMPANY

Founded 1848

160 Front Street, New York 7, N. Y.